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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

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Methods For Electrically Forming Materials; And Mixed
Metal Materials

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Methods for Electrically Forming Materials; And Mixed Metal Materials**TECHNICAL FIELD**

5 The invention pertains to methods of electrically forming materials comprising at least two elements, and in particular applications pertains to methods of forming materials comprising tantalum and titanium. The invention also pertains to mixed metal materials, such as materials comprising tantalum and titanium. In addition, the invention pertains to sputtering targets made of mixed metal materials, such as targets comprising tantalum and titanium.

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BACKGROUND OF THE INVENTION

Numerous applications exist in which it can be desired to form materials comprising two or more elements provided in a substantially homogenous distribution of the elements. For instance, it can be desired to form physical vapor deposition (PVD) targets comprising two or more metallic elements uniformly distributed throughout the targets. Frequently, it is difficult to combine two or more elements into a homogenous mixture when their melting points and/or densities are far apart. For example, there could be an interest to develop an alloyed titanium-tantalum target. However, making an alloyed titanium-tantalum ingot is impractical with conventional techniques. A large difference between the melting points of titanium and tantalum (1670°C for titanium and 2996°C for tantalum) makes it impractical to melt titanium together with tantalum in an e-beam furnace. Titanium would be simply vaporized at the melting point of tantalum. In addition, the large difference in densities (4.5g/cm³ for titanium and 16g/cm³ for tantalum) would be troublesome when powder processing an alloy comprising both titanium and tantalum. Segregation could too easily take place. Additionally, because of a generally higher gas content, powder processed targets are less preferred than melted and wrought targets.



It would be desirable to develop new methods for forming mixed metal alloy ingots, and it would be particularly desirable to develop methods which could be utilized to form titanium and tantalum alloy ingots. More generally, it would be desirable to develop new methods for forming products comprising mixtures of two or more elements. It is known that if an alloyed feedstock is melted, the melting point of the feedstock is between the melting points of components. Specifically, if an alloyed titanium and tantalum piece were melted, it would melt at a temperature in between the melting points of titanium and tantalum. The higher the portion of titanium in the piece, the lower would be the melting temperature. The lowering of the melting temperature could make the melting process much easier than for a material comprising pure tantalum. Therefore, it could be desirable to develop new methods for preparing tantalum materials diluted with titanium to form alloyed tantalum feedstocks for melting processes.

15 SUMMARY OF THE INVENTION

In one aspect, the invention encompasses a method of forming a material which comprises at least two elements. More specifically, the method comprises providing an electrolytic cell comprising a cathode, an anode, and an electrolytic solution extending between the cathode and anode. A metallic product is electrolytically formed within the electrolytic cell. The forming of the metallic product comprises primarily electrorefining of a first element of the at least two elements and primarily electrowinning of a second element of the at least two elements.

In another aspect, the invention encompasses a method for electrolytically forming a material, wherein an electrolytic cell is provided which comprises a cathode, at least two anodes, and an electrolytic solution extending between the cathode and the at least two anodes. The at least two anodes comprise first and second anodes having different concentrations of a first element relative to another. The electrolytic solution comprises a compound which includes a second element. A metallic product is

electrolytically formed with the electrolytic cell. The metallic product comprises a mixture of the first and second elements.

In yet another aspect, the invention encompasses a method for electrolytically forming a product which comprises a mixture of tantalum and titanium.

- 5 In yet another aspect, the invention encompasses a mixed metal product comprising at least two elements, such as a product comprising tantalum and titanium. The product comprising a mixture of the at least two elements can be considered an alloyed product, and can be used as feedstock for melting processes. In particular, a product comprising titanium and tantalum can be melted in an e-beam furnace to form a
- 10 titanium-tantalum alloy ingot for further processing into a sputtering target.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

- 15 Fig. 1 is a diagrammatic, cross-sectional view of an apparatus which can be utilized for methodology of the present invention.

Fig. 2 is a diagrammatic, cross-sectional view of a second apparatus which can be utilized for methodology of the present invention.

- 20 Fig. 3 is a diagrammatic, cross-sectional view of a sputtering target/backing plate structure which can be formed in accordance with methodology of the present invention.

Fig. 4 is a diagrammatic top view of the structure of Fig. 3, with the cross-sectional view of Fig. 3 indicated by the line 3-3 of the figure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 25 In one aspect, the invention encompasses a method of forming a mixed-metal product by electrolysis wherein one metal of mixed-metal product is formed by electrowinning and another metal of the product is formed by electrorefining. For purposes of interpreting this disclosure and the claims that follow, the term



“electrorefining” is defined to refer to a process in which a metal is transferred from an anode of an electrolytic apparatus to a cathode. Accordingly, electrorefining encompasses dissolution of a metal at an anode and deposition of the same metal at a cathode. In contrast, the term “electrowinning” is defined as a process wherein metal is transferred from electrolyte to a cathode. Accordingly, an electrowinning process does not require dissolution of a metal from an anodic material.

A process of the present invention is described with reference to Fig. 1. Specifically, Fig. 1 illustrates an exemplary electrolytic cell 10 comprising a cathode 12 and anode 14 which are electrically connected through a power source (not shown) to provide a potential difference 16 (i.e., a voltage) between the anode and cathode. Electrolytic cell 10 further comprises a vessel 18 which retains an electrolyte solution 20 therein. Vessel 18 comprises a furnace 22 and a liner 24 on an interior surface of furnace 22. Liner 24 can comprise, for example, graphite. Furnace 22 is utilized to maintain electrolytic solution 20 above a melting temperature of the solution, and further can be utilized to maintain a substantially constant temperature during an electrolytic process of the present invention. Electrolytic solution 20 extends between cathode 12 and anode 14, and accordingly completes an electrical circuit comprising cathode 12 and anode 14.

A reactant material 26 is shown joined with anode 14. Reactant material 26 can comprise a first metallic element. Although the shown embodiment has reactant material 26 provided as a discrete material relative to anode 14, it is to be understood that material 26 and anode 14 can comprise a one-piece construction, with anode 14 having a substantially homogenous composition of the first element. If the reactant material 26 is provided as a separate piece from the remainder of anode 14, reactant material 26 can be joined to the remainder of anode 14 through a conductive interface, such as, for example, through a conductive epoxy, or a welded, brazed, or solid-diffused joint. In alternative embodiments, the anode 14 can have a cupped shape, and material 26 can be retained within the cupped shape. For instance, anode 14 can be configured as a basket. In other embodiments, liner 24 can be utilized as the anode, and material 26 can be provided on

the bottom of vessel 18 and lying in electrical connection with liner 24. As long as material 26 is in electrical connection with the remainder of an anodic material, material 26 can be considered as being part of an anode during an electrolytic operation.

Accordingly, electrolytic operation will comprise consumption of material from anodic component 26 and redeposition of the material onto cathode 12. In other words, the electrolytic operation will comprise electrorefining of material from anodic component 26.

In the shown embodiment, a product 28 is illustrated being formed around a portion of cathode 12. Cathode 12 preferably comprises a material which is non-reactive with product 28, so that product 28 can be readily removed from cathode 12 after an electrolytic process. To reduce contamination in the cathode deposit, it can be preferred to use the same or a similar material as the cathode material. In particular applications, cathode 12 can comprise, for example, a titanium rod.

Although product 28 is shown formed on cathode 12 in the illustrated process, it is to be understood that the invention encompasses other embodiments wherein material 28 is formed relative to cathode 12 and then shed from the cathode. In such embodiments, material 28 can be collected on a shelf (not shown) provided beneath cathode 12, or in a basket (not shown) surrounding a portion of cathode 12.

Electrolytic solution 20 comprises an element different from the element which is electrorefined from anode 26. The element electrorefined from anode 26 can be considered a first element, and the different element in electrolytic solution 20 can be considered a second element. The second element can be provided as a compound within electrolytic solution 20, and in particular embodiments can be provided as a salt. The second element is transferred from solution 20 to product 28, and accordingly is electrowon during the electrolytic operation of apparatus 10. The first and second elements transferred to product 28 are typically metals, and accordingly product 28 can be a mixed-metal product comprising a first metal formed by an electrorefining process and a second metal formed by an electrowinning process.



The first and second metals of product 28 may not be formed entirely by the electrorefining and electrowinning processes, respectively. If anode 26 comprises a mixture of both elements and the electrolytic process is operated at a cell voltage sufficiently large for both metals to be anodically dissolved and cathodically deposited, an amount of the second element formed within product 28 will result from an electrorefining process. Also, if there are contaminants containing the first element within electrolyte 20, an amount of the first element within product 28 will result from the electrowinning process. To account for such contributions of electrorefining and electrowinning, product 28 can be described as being formed by primarily electrorefining of the first element from anode 26 and by primarily electrowinning of the second element from electrolyte 20. In such description, the term "primarily" indicates that there may be some electrowinning of the first element and some electrorefining of the second element.

Although product 28 is described as comprising as a mixture of two elements, it is to be understood that product 28 can also comprise mixtures of more than two elements. For example, a mixture of elements can be provided in anodic component 26 so that more than one element is electrorefined and formed in product 28 with the electrowon element from electrolyte 20. Alternatively, or additionally, more than one element can be provided within electrolyte 20 to be electrowon during the electrorefining of one or more elements from anodic component 26. The mixed elements of product 28 will typically together define an alloy composition.

Processing of the present invention can be utilized to form materials 28 comprising mixtures of numerous elements. For instance, product 28 can comprise, consist of, or consist essentially of, two or more of tantalum, titanium, hafnium, zirconium and niobium. Alternatively, product 28 can comprise, consist of, or consist essentially of at least one of tantalum, titanium, hafnium, zirconium and niobium in combination with at least one of vanadium, aluminum, chromium, and nickel. In exemplary applications, product 28 can comprise a mixture of tantalum and titanium;

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 2. *Medical Devices*
 3. *Biotechnology*
 4. *Health Insurance*
 5. *Hospitals*
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 93. *Biotechnology*
 94. *Health Insurance*
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 96. *Pharmaceuticals*
 97. *Medical Devices*
 98. *Biotechnology*
 99. *Health Insurance*
 100. *Hospitals*

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5% zirconium to about 95% zirconium; from about 5% to about 25% zirconium; from about 25% to about 50% zirconium; from about 50% to about 75% zirconium; or from about 75% to about 95% zirconium.

In yet other particular applications, product 28 can consist of, or consist essentially of, mixtures of niobium and other materials selected from the group consisting of one or more of hafnium, zirconium, titanium, vanadium, aluminum, chromium, nickel, and tantalum. Such product can comprise, for example, from about 5% niobium to about 95% niobium; from about 5% to about 25% niobium; from about 25% to about 50% niobium; from about 50% to about 75% niobium; or from about 75% to about 95% niobium.

In an exemplary embodiment of the present invention, product 28 comprises a mixture of tantalum and titanium, wherein titanium is the electrorefined element and tantalum is the electrowon element. In such embodiment, titanium will be provided as an anodic material, and a tantalum-containing compound will be provided within electrolyte 20. The tantalum-containing compound can be a salt, such as, for example, K_2TaF_7 . The titanium material of the anode can comprise relatively pure titanium, such as, for example, a material which is at least 99.9% titanium. Alternatively, the material can be a relatively impure form of titanium, and the electrolytic process can be utilized to purify the titanium during the electrorefining of the titanium and concomitant formation of titanium within product 28.

Electrolyte solution 20 is preferably maintained at a temperature of from about 600°C to about 850°C, and more preferably from about 700°C to about 750°C, during formation of a titanium/tantalum product 28.

A relative ratio of the first and second elements to one another within product 28 can be influenced and controlled by various parameters. For example, the concentration ratio of the first element to the second element in electrolyte 20 can alter the relative proportions of the first and second elements in product 28. Also the temperature of electrolyte 20 can influence the kinetics of various half reactions in the cell and thus alter

the relative proportions of the first and second elements in product 28. Another method to control the relative ratio of the first and second elements to one another within product 28 is described below as a second embodiment with reference to Fig. 2.

Fig. 2 illustrates an apparatus 50 comprising a cathode 52 and a pair of anodes 54 and 56. Apparatus 50 further includes a vessel 58 comprising a furnace 80 and a liner 62; with an electrolyte solution 64 shown contained within vessel 58. Vessel 58 can comprise a construction identical to that described above with reference to vessel 18 of Fig. 1. Cathode 52 can comprise a construction identical to that described above with reference to cathode 12, and anode 54 can comprise a construction identical to that described above with reference to anode 14. The difference between the apparatus 50 of Fig. 2 and the apparatus 10 of Fig. 1 is that apparatus 50 comprises a second anode 56, in addition to the first anode 54. Anode 54 is coupled to cathode 52 to a first voltage (or potential) 68, and anode 56 is coupled to cathode 52 to a second voltage 70.

In the shown construction, first anode 54 is coupled with a reactant material 66 which is to be electrorefined during electrolytic operation of apparatus 50. Anode 56, in contrast, is not coupled with a reactant material. It is to be understood, however, that the invention encompasses other embodiments (not shown) wherein anode 56 is coupled with a reactant material. Preferably, in such constructions the reactant material coupled with anode 56 will have a different concentration of an element that is to be electrorefined than does the reactant material 66.

Electrolyte 64, like the electrolyte 20 of the Fig. 1 apparatus, comprises an element which is to be electrowon during electrolytic operation of apparatus 50. In an exemplary application, this element can be tantalum, and the reactant anodic material 66 can comprise titanium.

In operation, power is supplied to generate potentials 68 and 70, and such causes electrorefining of an element from anodic material 66 and electrowinning of an element from electrolyte 64. The electrowon and electrorefined elements together form a product



72. The relative concentration of the electrowon and electrorefined materials can be adjusted by adjusting voltage 68 relative to voltage 70.

In particular embodiments of the present invention, second anode 56 comprises graphite, and the first anode comprises a titanium material, such as, for example, a titanium reactant 66. (It is noted that although anodic reactant 66 is shown separately coupled to anodic component 54, the invention encompasses alternative embodiments (not shown) wherein anodic component 54 itself comprises the titanium material, and wherein the separate anodic material 66 is not utilized).

Generally, voltage 68 and voltage 70 are determined by the desired half reactions at each anode and at cathode. In an exemplary case, the desired half reaction at anode 54 is $\text{Ti} - 2 e = \text{Ti}^{2+}$; whereas at anode 56 a reaction of fluorine gas generation is desired: $2\text{F}^- - 2 e = \text{F}_2$. At the cathode, two reaction are desirable: $\text{Ti}^{2+} + 2 e = \text{Ti}$ and $\text{Ta}^{5+} + 5 e = \text{Ta}$. Voltage 68 and voltage 70 should be large enough to ensure that these reactions take place. The relative magnitude of voltage 68 to voltage 70 can dictate the amount of titanium transferred to product 72. Specifically, if the magnitude of voltage 68 is reduced relative to the magnitude of voltage 70, less titanium will be transferred to product 72. Accordingly, a relative concentration of tantalum in material 72 can be decreased by decreasing the magnitude of voltage 68 relative to the magnitude of voltage 70. In particular applications, the magnitude of voltage 68 relative to voltage 70 will be fixed during formation of product 72. In other applications, the magnitude of voltage 68 will be varied relative to the magnitude of voltage 70 during product formation, and such can cause a relative concentration of tantalum and titanium to be varied within product 72.

In particular embodiments, first anode 54 and second anode 56 can both comprise titanium, but at different concentrations relative to one another. In such applications, the relative concentration of titanium in material 72 can still be adjusted by adjusting the potential 68 relative to the potential 70. Specifically, if anode 54 comprises a higher concentration of titanium than anode 56, then a higher relative magnitude of potential 68



to potential 70 will result in more titanium being electrorefined in product 72 than would be electrorefined with a lower relative magnitude of potential 68 to potential 70.

In still other particular embodiments of the present invention, anode 56 will not comprise an element which is to be electrorefined, but will instead comprise, for example, carbon, and will therefore be utilized for electrowinning only. For instance, anode 56 can predominantly comprise carbon (for example, graphite), consist essentially of carbon, or consist of carbon.

Although the embodiment of Fig. 2 is described as forming a mixed metal product comprising two different elements, it is to be understood that the embodiment can be utilized for forming mixed metal products comprising more than two elements. For instance, multiple elements can be electrorefined and combined with an electrowon element to form product 72. Alternatively, multiple elements can be electrowon and combined with an electrorefined element. In yet other alternative embodiments, multiple materials can be electrorefined and combined with multiple materials which are simultaneously electrowon to form the resultant product.

Once a mixed metal product is formed (either 28 of Fig. 1 or 72 of Fig. 2, for example) the mixed metal product can be subjected to further processing to yield a material suitable for industrial applications. For instance, the mixed metal product can be melted and cast into an ingot form. Since the mixed metal product is formed by co-deposition of two or more metals, it is essentially microscopically homogeneous and the deposition process can be, in fact, an alloying process. The melting point of the alloyed mixed metal product will be between the melting points of the constituent metal elements. For a mixed titanium-tantalum product, this means that it will melt below 2996°C, but above 1670°C. The actual melting temperature is dependent on the proportions of both elements. A lower melting temperature can make a melting process much easier. Accordingly, a mixed metal product of this invention comprising a titanium/tantalum alloy can be a more suitable feedstock for melting and forming

tantalum-containing ingots than would be a material comprising pure tantalum or a material mixture comprising pure tantalum and pure titanium in a non-alloyed state.

The relative amount of tantalum and titanium in product 28 (or product 72), and in melted ingots formed from the product, can be adjusted so that either titanium or tantalum is the predominant material. Further product 28 or melted ingots can consist essentially of, or consist of, titanium and tantalum. Ingots can be subjected to metallurgical processing (such as, for example, hot forging, hot or cold rolling, extrusion and thermal treatments,) to adjust textures and/or grain sizes within the materials of the ingots to desired parameters. Attention should be paid to the solubility of tantalum in titanium during metallurgical processing. The solubility of tantalum in titanium at 600°C is about 12%. It reduces during cooling, and is, for example, only about 7% at 400°C. Thus, tantalum-rich precipitates can form during cooling from a melting temperature or another higher processing temperature, when tantalum exceeds its solubility in titanium. In alloys with a low tantalum content, this is not a problem. But for higher tantalum content, say higher than 7%, the precipitation could be undesirable. A method of reducing precipitate formation is to rapidly quench the titanium/tantalum mixed metal product so that the tantalum is locked within the titanium matrix before the tantalum has an opportunity to form precipitates. The temperature and rate of the quench procedure are preferably chosen such that there is effectively no tantalum-rich precipitate present within the titanium/tantalum material after it has been quenched. A suitable fluid for quenching the titanium/tantalum material is a liquid, such as, for example, water or oil.

Another way to prevent or reduce precipitation is to apply powder metallurgy to form parts. The mixed metal product 28 or 72 is essentially free of segregation. When pressed into shapes and sintered at a suitable temperature, parts can be free of precipitates and free of segregation. Therefore, the mixed metal product 28 or 72 can be considered a better starting material for a powder process than would be a material having a higher amount of segregation between elemental constituents of the material.

The discussion above is directed toward forming titanium/tantalum materials predominately comprising titanium and having effectively no tantalum-rich precipitates therein. Methodology of the present invention can also be utilized to form titanium materials having tantalum-rich precipitates therein. Such materials can be formed if a
5 tantalum concentration exceeds the solubility of tantalum in titanium. A suitable thermomechanical process including forging, and/or rolling, and/or extrusion, and heat treatment can be performed to control the size, the shape and the distribution of the tantalum-rich precipitates.

The thermo-mechanically processed material can then be shaped into a form
10 suitable for desired industrial applications. For instance, the material can be shaped into a PVD target, such as, for example, a sputtering target.

Figs. 3 and 4 illustrate exemplary embodiments of a PVD target assembly. Specifically, Figs. 3 and 4 illustrate an assembly 100 comprising a sputtering target 102 bonded to a backing plate 104. The shown construction is an ENDURA™ construction,
15 but it is to be understood that the invention can be utilized for forming other PVD target constructions. Further, although the shown embodiment has a sputtering target 102 bonded to a backing plate 104, it is to be understood that the invention also encompasses embodiments wherein the mixed metal target is a monolithic target. In such
20 100, and accordingly wherein there is no backing plate 104. The mixed metal product can be formed into a target shape (such as, for example, the shape of target 102; or the shape of a monolithic target) by conventional metal-working methodology.

It can be advantageous to have a target 102 comprising a mixture of tantalum and titanium. For instance, PVD targets are frequently utilized for sputter deposition of
25 tantalum in forming semiconductor constructions. Tantalum can be a desired barrier layer in constructions comprising copper, in that tantalum can impede copper diffusion. However, tantalum is a relatively expensive material. Accordingly, it can be desired to

form targets wherein tantalum is diluted within another, less expensive, material; and then to sputter-deposit tantalum-containing films from such targets.

It can be advantageous to utilize methodology of the present invention for forming products comprising mixtures of titanium and tantalum, in that it is typically difficult to mix tantalum and titanium. Specifically, tantalum and titanium have significantly different melting points from one another (1670°C for titanium and 2996°C for tantalum) and significantly different densities (4.5 grams/centimeter³ for titanium and 16 grams/centimeter³ for tantalum). Accordingly, segregation between titanium and tantalum frequently happens during either melting or powder processing of titanium and tantalum in attempts to form mixtures of titanium and tantalum by conventional methodology. However, methodology of the present invention can form products comprising mixtures of titanium and tantalum with little or no segregation of titanium and tantalum within the products.

Exemplary targets comprising tantalum diluted in another material are targets comprising a mixture of tantalum and titanium. In particular applications, such targets can consist essentially of a mixture of tantalum and titanium, and in further applications such targets can consist of a mixture of tantalum and titanium. Further, the targets can be provided to a purity of 99.9% (3N) or higher (with the percentage being expressed in terms of weight percent; and with it being understood that percentage purities expressed herein are in terms of weight percent unless stated otherwise), with desired purities being 99.99%, 99.995%, 99.999%, 99.9995%, or higher. Such purities can be obtained by methodology of the present invention, in that electrorefining and electrowinning methodology of the present invention can be utilized as a purification step, in addition to a step involved in formation of a mixed metal product. Further, if it is desired to increase a purity of a mixed metal product, such can be accomplished utilizing conventional processes, such as, for example, e-beam melting.

In particular applications, a sputtering target of the present invention will comprise tantalum and titanium; consist of tantalum and titanium, or consist essentially

comprise titanium to a concentration of at least about 50%, and can comprise tantalum to a concentration of less than or equal to about 50%. In other alternative embodiments, the target can comprise more than 50% tantalum, with the remainder of the target being titanium; with an exemplary PVD target consisting of tantalum and titanium, and having a tantalum concentration greater than or equal to about 5 weight percent and less than or equal to about 95 weight percent.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



APPLICATION FOR LETTERS PATENT

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Methods of Forming Titanium-Based and Zirconium-
Based Mixed-Metal Materials; and Sputtering Targets

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Methods Of Forming Titanium-Based And Zirconium-Based Mixed-Metal Materials; And Sputtering Targets

TECHNICAL FIELD

5 The invention pertains to methods of forming titanium-based mixed-metal materials and zirconium-based mixed-metal materials. The invention also pertains to sputtering targets, and in particular applications pertains to zirconium-containing sputtering targets and/or titanium-containing sputtering targets.

10 BACKGROUND OF THE INVENTION

 There are numerous applications in which it can be desired to form mixed-metal products. For purposes of interpreting this disclosure and the claims that follow, the terms "alloy" and "mixed-metal product" are both defined to pertain to compositions having at least two elements present to amounts greater than or equal to the sum of any
15 metallic impurities. For example, a material that is 4N5 pure (i.e., 99.995% pure) has a total of all metallic impurities of 50 ppm or less. A 4N5 alloy (or mixed-metal product) of Ti and Zr is defined herein to comprise both Ti and Zr in amounts greater than or equal to 50 ppm. Typically, one of the Ti and Zr would be present in much higher concentration than the other, but regardless, both would be present in concentrations
20 greater than that of the total metallic impurities. Other exemplary mixed-metal materials are a 3N5 mixed-metal material, which, in accordance with the definition herein comprises at least two elements that are each present to a concentration in excess of 500 ppm; and a 5N5 mixed-metal material, which, in accordance with the definition herein comprises at least two elements which are each present to a concentration in excess of
25 5 ppm. The percentages and concentrations referred to herein are weight percentages and concentrations, except, of course, for any concentrations and percentages specifically indicated to be other than weight percentages or concentrations.

 Among the applications for which it can be desired to form a mixed-metal product or alloy are applications in which it is desired to form ingots of high purity

alloys. It can be desired to form ingots of high purity alloys to enable formation of sputtering targets (also referred to as physical vapor deposition targets) from the ingots. The sputtering targets will have uniform distribution of alloys throughout as a result of being formed from ingots consisting of a uniform composition of high purity alloys.

5 Typically, alloys are made by either adding elemental alloy components to a molten pool of bulk metal, or by pre-mixing and blending various melt feedstock materials with one another before actually melting the materials together. A limitation of the above-described processes is that the processes do not lend themselves to a batch melting process in that at no time is the whole of an ingot material simultaneously
10 molten. Because of this, several consecutive melting operations must be performed in order to form a uniform refractory metal alloy. Without multiple melting operations, variations in chemical composition form in a resulting ingot material. Such variations in chemical composition can lead to problems in structures formed from the ingot materials. For instance, if sputtering targets are formed from the ingot materials, the sputtering
15 targets can have non-uniform chemical compositions reflecting the non-uniform chemical composition within the ingot. If the sputtering targets are utilized in semiconductor fabrication, material will be sputtered from the targets to deposit a film on a semiconductive substrate. Ideally, the film will be homogeneous and uniform across the material. However, variations in chemical composition and homogeneity within a
20 sputtering target can translate into variations in composition and homogeneity of a deposited film, and reduce quality of devices comprising the film.

For the above-discussed reasons, it is desired to develop methodology for forming ingots having uniform and homogeneous composition throughout.

Another aspect of the prior art is that integrated circuit interconnect technology is
25 changing from aluminum subtractive processes to copper dual damascene processes. The shift from aluminum to copper is causing new barrier layer materials to be developed. Specifically, titanium nitride (TiN) films had been utilized as barrier layers in the aluminum technologies to inhibit aluminum atoms from diffusing into adjacent dielectric materials and causing device failure. The TiN films can be formed by, for

example, reactively sputtering a titanium target in a nitrogen atmosphere. The TiN films are found to be poor barrier layers relative to copper because the diffusivity of copper atoms through TiN films is too high.

Another problem that can occur in attempting to utilize titanium materials as barrier layers can occur in attempting to adhere titanium materials to dielectric materials. Specifically, it is often found that titanium materials adhere poorly to commonly used dielectric materials (such as, for example, silicon dioxide), and that circuit defects can be caused by such poor adhesion.

In an effort to avoid the problems associated with titanium, there has been development of non-titanium barrier materials for diffusion layers. Among the materials which have been developed is tantalum nitride (TaN). It is found that TaN can have a close to nanometer-sized grain structure and good chemical stability as a barrier layer for preventing copper diffusion. However, a difficulty associated with TaN is that the high cost of tantalum can make it difficult to economically incorporate TaN layers into semiconductor fabrication processes.

Titanium can be a lower cost material than tantalum. Accordingly, it could be possible to reduce materials cost for the microelectronics industry relative to utilization of copper interconnect technology if methodology could be developed for utilizing titanium-comprising materials, instead of tantalum-comprising materials, as barrier layers for inhibiting copper diffusion. It is therefore desirable to develop new titanium-containing materials which are suitable as barrier layers for impeding or preventing copper diffusion, and to develop methodology for forming sputtering targets comprising the new materials.

In addition to the desirability of developing new titanium-containing materials which are suitable as barrier layers, it would also be desirable to develop other materials suitable as barrier layers and having either lower cost or better properties than the tantalum materials presently being utilized. Further, it would be desirable to develop methodology for forming sputtering targets comprising such other materials.

SUMMARY OF THE INVENTION

In one aspect, the invention encompasses a method of forming a titanium-based or zirconium-based mixed-metal material. For purposes of interpreting this disclosure and the claims that follow, a "titanium-based" material is defined as a material in which titanium is a majority element, and a "zirconium-based" material is defined as a material in which zirconium is a majority element. A "majority element" is defined as an element which is present in larger concentration than any other element of a material. A majority element can be a predominate element of a material, but can also be present as less than 50% of a material. For instance, titanium can be a majority element of a material in which the titanium is present to only 30%, provided that no other element is present in the material to a concentration of greater than or equal to 30%. In an exemplary process of forming a titanium-based mixed-metal ingot, such ingot can be formed by combining a mixture of titanium halide and at least one other metal halide with a reducing agent to produce a mixed-metal product. The mixed-metal product is then melted to form a molten mixed-metal material. The molten mixed-metal material is cooled into a mixed-metal ingot. The ingot comprises titanium and at least one other metal. The titanium is the majority element of the ingot, the ingot has a purity of titanium and the at least one other metal of at least 99.95%. The method can be utilized for forming a zirconium-based material by substituting zirconium halide for the titanium halide.

In another aspect, the invention encompasses a method of electrolytically forming a titanium-based mixed-metal material. A mixture of titanium and at least one other metal is electrically deposited as a mixed-metal product. The mixed-metal product is melted to form a molten mixed-metal material. The molten mixed-metal material can be cooled into a mixed-metal ingot. The ingot comprises the titanium and the at least one other metal. The titanium is the majority element of the ingot, and the ingot has a purity of titanium and the at least one other metal of at least 99.95%. The method can be utilized for electrolytically forming a zirconium-based mixed-metal ingot by substituting zirconium for the titanium.

In another aspect, the invention encompasses an iodide transfer method of forming a titanium or zirconium-based mixed-metal material. A mixture comprising either titanium or zirconium is provided in a reaction apparatus with iodine gas and a heated substrate. The titanium or zirconium is reacted with the iodine gas to form an iodide which is subsequently transferred to the heated substrate. Heat from the substrate is utilized to decompose the iodide and produce a mixed-metal product comprising the titanium or zirconium. The mixed-metal product can be melted to form a molten mixed-metal material which can then be cooled into a mixed-metal ingot.

In yet another aspect, the invention encompasses a sputtering target comprising zirconium and one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb.

In yet another aspect, the invention encompasses a sputtering target comprising titanium and boron.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a flow-chart diagram illustrating methodology encompassed by the present invention.

Fig. 2 is a flow-chart diagram illustrating an exemplary reduction process of the present invention.

Fig. 3 is a diagrammatic, cross-sectional view of an apparatus utilized in an electrolytic process of the present invention.

Fig. 4 illustrates a graph showing standard reduction potential for a series of elements, and further showing a window region encompassing elements having a standard reduction potential within ± 0.5 volt of the Ti^{2+}/Ti reaction.

Fig. 5 is a diagrammatic, cross-sectional view of an iodide process encompassed by the present invention.

Fig. 6 is a block diagram of a melting and ingot-forming process encompassed by the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The invention includes new methods for forming mixed-metal materials, and in particular applications encompasses new methods of forming ingots comprising mixtures of metals. In particular embodiments, a mixed-metal feedstock is produced by one or more of a reduction process, electrolysis process or iodide process, and such feedstock is subsequently melted to form a homogeneous molten mixture of the metals. The molten
10 mixture is then cooled to form a mixed-metal ingot, with the metals being homogeneously mixed throughout the ingot as, for example, an alloy composition. The ingot can be subsequently utilized to form materials in which homogeneous mixed-metal compositions are desired. For instance, the ingot can be utilized in forming sputtering targets. It is noted that various reduction processes, electrolysis processes and iodide
15 processes have been described previously in U.S. Patent Nos. 6,063,254, and 6,024,847; and in U.S. Patent Application Serial No. 08/994,733. U.S. Patent Nos. 6,063,254, and 6,024,847, and U.S. Patent Application Serial No. 08/994,733 are all incorporated herein by reference.

 In particular applications, the mixed-metals provided within the ingot will be
20 titanium-based materials (i.e. titanium will be a majority element within the metals), and in other applications the mixed-metals will be zirconium-based mixtures (i.e. zirconium will be a majority element within the metals). Either titanium-based mixtures or zirconium-based mixtures can ultimately be utilized in forming sputtering targets. A use for a titanium-based sputtering target or a zirconium-based sputtering target can be for
25 sputter-deposition of a titanium-based or zirconium-based film on a semiconductor substrate. Either a titanium-based film or a zirconium-based film can be utilized as a barrier layer to impede copper migration from copper-containing components to other components associated with the semiconductor substrate. Specifically, the film can be provided between a copper-containing component and other components of a

semiconductor substrate, and can be utilized to prevent copper migration from the copper-containing component to the other component associated with the substrate. To aid in interpretation of the claims that follow, the terms "semiconductive substrate" and "semiconductor substrate" are defined to mean any construction comprising

5 semiconductor material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive structures described above. An exemplary
10 semiconductive material is silicon, such as, for example, monocrystalline silicon. Among the titanium-based barrier layers that can be particularly useful are layers comprising, consisting essentially of, or consisting of titanium and one or both of Zr and Hf; and such layers can be formed from sputtering targets comprising, consisting essentially of, or consisting of titanium and one or both of Zr and Hf. Among the
15 zirconium-based barrier layers that can be particularly useful are layers comprising, consisting essentially of, or consisting of zirconium and one or both of Ti and Hf; and such layers can be formed from sputtering targets comprising, consisting essentially of, or consisting of zirconium and one or both of Ti and Hf.

A method encompassed by the present invention is shown in the flow chart of
20 Fig. 1. At an initial step 10, a mixture of metallic elements is provided. The mixture will typically comprise titanium or zirconium, and in particular embodiments can comprise both titanium and zirconium. The elements can be in an elemental form in the mixture of step 10, or can be provided as molecular components. For instance, titanium can be provided as, for example, elemental Ti or TiCl_4 .

25 The mixture of step 10 is provided to one or more of a reduction process 12, an electrolysis process 14, or an iodide process 16. In the diagram of Fig. 1, the reduction process 12 is shown connected through a dashed arrow to electrolysis process 14, which in turn is shown connected through a dashed arrow to iodide process 16. The dashed arrows show that the processes 12, 14 and 16 can be optionally conducted sequentially

relative to one another. For instance, a material from step 10 can be provided to reduction process 12, and then subsequently provided from reduction process 12 to electrolysis process 14, and subsequently provided from electrolysis process 14 to iodide process 16. Alternatively, the material from step 10 can be provided to reduction process 12, and then not submitted to either electrolysis process 14 or iodide process 16. Further, although the arrows between processes 12, 14 and 16 are shown proceeding in particular directions, it is to be understood that the processes connected by the dashed arrows can be connected in reverse to the shown methodology. For instance, material from electrolysis process 14 can be provided to reduction process 12, rather than the shown flow proceeding from reduction process 12 to electrolysis process 14. However, the shown flow can be a preferred flow orientation, in that the electrolysis process is generally considered to be a process for further purification of material after a reduction process, and the iodide process is considered to be a process which can lead to additional purification beyond that accomplished by either electrolysis process 14 or reduction process 12.

After the flow of material through one or more of processes 12, 14 and 16, the material is considered a product. The product is subjected to the processing of step 18, which comprises melting the product, and subsequently cooling the molten material to form an ingot. The ingot will have a mixture of elements contained therein, with such mixture reflecting at least some of the original mixture of metallic elements utilized in the composition of step 10. However, the final composition formed in the ingot of step 18 may have a different stoichiometric relationship of component elements than the mixture of step 10, as the kinetics and/or thermodynamics of processes 12, 14 and 16 may favor one metallic material relative to another.

The processes of steps 12, 14, 16 and 18 are described in more detail in Figs. 2-6. Referring initially to Fig. 2, the reduction process of step 12 is further illustrated. The shown process forms a mixed-metal material consisting essentially of, or consisting of, a titanium/zirconium alloy. Initially, zirconium tetrachloride (ZrCl_4), titanium tetrachloride (TiCl_4), and a reductant (for example, sodium or magnesium metal) are

mixed. A resulting exothermic reaction produces an alloy of titanium and zirconium. The relative proportions of titanium and zirconium within the alloy are approximately proportional to the proportions of zirconium tetrachloride and titanium tetrachloride. Accordingly, a titanium-based alloy can be formed by utilizing a higher proportion of titanium tetrachloride relative to zirconium tetrachloride, and a zirconium-based alloy can be formed by utilizing a higher percentage of zirconium tetrachloride relative to titanium tetrachloride. Although the invention is described with reference to an embodiment utilizing metal chloride reactants, it is to be understood that other metal halides can be utilized in addition to, or alternatively to, the metal chlorides.

10 The reactants utilized in the reduction process of Fig. 2 will typically be in a gaseous or liquid form. For instance, the reductant can comprise molten sodium and the zirconium tetrachloride and titanium tetrachloride can be in gaseous form. Accordingly, the reactions occurring in the reduction process can be summarized as reactions (1) and (2) below, in which s = solid phase; l = liquid phase and g = gas phase.

15



20 The Ti(s) and Zr(s) can form a mixed-metal sponge. Such sponge can be subsequently melted and cooled to form an ingot, or can be utilized as a feedstock in either the electrolytic process 14 of Fig. 1 or the iodide process 16 of Fig. 1.

25 Although the reduction process is illustrated in Fig. 2 as being a process for forming an alloy consisting of titanium and zirconium, it is to be understood that the reduction process can form other metal materials. For instance, one or more metals selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr, can be utilized in combination with the titanium to form an alloy. More specifically, chlorides (or other halides) of the listed elements can be utilized in combination with titanium tetrachloride to form alloys in the reduction process. Alternatively, one or more

elements from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb can be utilized in combination with the zirconium to form an alloy.

If the formed alloy is a titanium-based alloy, then the total non-titanium metal content of a material produced by the process of Fig. 1 can be in a range of from 0.001% to 50%, such as, for example, a range of from 0.001% to 10%. In particular embodiments, the total non-titanium metal content of the material will be at least 0.01%, in further embodiments will be at least 0.1%, in yet other embodiments will be at least 1%, and in yet other embodiments will be at least 2%. The amount of at least one non-titanium metal in the mixed-metal material will be provided to a sufficient concentration in the material to present to greater than 5 ppm in a material pure to 5N5, greater 50 ppm in a material pure to 4N5, greater than 500 ppm in a material pure to 3N5, or greater than one part per thousand in a material pure to 3N.

If the mixed-metal material is subsequently melted and utilized to form an ingot as shown in step 18 of the Fig. 1 process, and if such melting occurs without intervening processes occurring between the reduction process and the melting process, the relative proportion of non-titanium metals in a formed ingot will be the same as that of the mixed-metal product formed by the reduction process of Fig. 2.

If the formed alloy is a zirconium-based alloy, then the total non-zirconium metal content of a material produced by the process of Fig. 1 can be in a range of from 0.001% to 50%, such as, for example, a range of from 0.001% to 10%. In particular embodiments, the total non-zirconium metal content of the material will be at least 0.01%, in further embodiments will be at least 0.1%, in yet other embodiments will be at least 1%, and in yet other embodiments will be at least 2%. The amount of at least one non-zirconium metal in the mixed-metal material will be provided to a sufficient concentration in the material to present to greater than 5 ppm in a material pure to 5N5, greater 50 ppm in a material pure to 4N5, greater than 500 ppm in a material pure to 3N5, or greater than one part per thousand in a material pure to 3N.

In particular embodiments, the reduction process of Fig. 2 can be utilized to form an alloy consisting of titanium and zirconium, as shown. In such processes, the material can be titanium-based, with the only other metal besides titanium being zirconium; or can be zirconium-based, with the only other metal besides zirconium being titanium.

5 Referring next to Fig. 3, the electrolysis process 14 of Fig. 1 is described in more detail. Specifically, Fig. 3 illustrates an apparatus 50 which can be utilized for an electrolytic procedure of the present invention. Apparatus 50 comprises a furnace 52. An anode 54 and cathode 56 are provided within furnace 52. A metal feedstock 58 is provided against anode 54. Metal feedstock 58 can comprise, for example, one or both
10 of titanium or zirconium. In particular embodiments, the metal feedstock can comprise titanium with at least one other metal selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr; or can comprise zirconium and at least one other metal selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La,
15 Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb. In an exemplary embodiment, titanium is a majority element provided in the feedstock, and in another exemplary embodiment zirconium is a majority element provided in the feedstock.

An electrolyte 60 is provided between the anode and the cathode. The electrolyte can comprise a salt, such as, for example, sodium chloride or magnesium chloride, and
20 can be in a molten form due to a temperature maintained by furnace 52.

In operation, an electrical voltage is provided between anode 54 and cathode 56, and metal is electrolytically transferred from mixture 58 to cathode 56 to form a mixed-metal product 62 at cathode 56. Although mixture 58 is described as being provided against an anode 54, it is to be understood that anode 54 can be considered an electrical
25 interconnection to mixture 58, and that mixture 58 can be considered to effectively be the "anode" during the electrolytic transfer reaction. The composition of mixed-metal product 62 can be determined, in part, by the voltage supplied to apparatus 50. Fig. 4 illustrates a chart of standard reduction potential for reduction of various elements. Fig. 4 also illustrates a window formed within ± 0.5 volt of the reduction for Ti^{2+}/Ti .

Accordingly, if a voltage supplied to apparatus 50 is within ± 0.5 volts of the reduction potential for Ti^{2+}/Ti , only the elements within the shown window will be formed in the mixed-metal product 62. Accordingly, apparatus 50 can be utilized for purification of a mixed-metal product relative to the material 58 provided at anode 54. The elements

5 having reduction potential within ± 0.5 volt of the reduction of Ti^{2+}/Ti include Eu, Zr, Ti, and Zn.

An aspect of the present invention is to form a mixed-metal product at cathode 56. For instance, if a majority element is titanium, then the material at cathode 56 will preferably comprise at least 0.001% of elements other than titanium; and

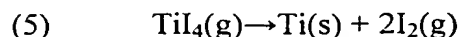
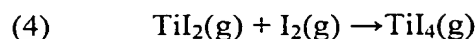
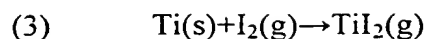
10 if a majority element is zirconium, then product 62 will preferably comprise at least 0.001% of elements other than zirconium. The amount and type of elements provided at cathode 56 can be determined by the voltage utilized for apparatus 50 and the starting material 58. Specifically, if a voltage window of ± 0.7 volts from the reduction potential for conversion of Ti^{2+}/Ti is utilized, a wider number of elements can be incorporated into

15 product 62 than if a voltage window of ± 0.5 volts from the reduction potential for conversion of Ti^{2+}/Ti is utilized. Preferably, a voltage window will not exceed more than ± 0.7 volts from the reduction potential for a majority element (for example, either titanium or zirconium), to avoid adding excessive impurity to product 62.

Referring next to Fig. 5, an iodide process which can be utilized for step 16 of

20 Fig. 1 is diagrammatically illustrated. Specifically, Fig. 5 shows an apparatus 100 comprising a reaction chamber 102. A feedstock 106 is provided within reaction chamber 102, and a heated substrate 104 extends into reaction chamber 102. Feedstock 106 comprises at least 2 different metals, and can, for example, comprise either titanium or zirconium as a majority metal. An iodine gas 108 is provided within

25 reaction chamber 102. In operation, iodine gas 108 transports metal from feedstock 106 to heated substrate 104. The metal is then deposited onto substrate 104 to form a product 110. The transport of a metal from feedstock 106 to heated substrate 104 is described below with reference to reactions (3)-(5), and specifically is described with respect to formation of a titanium metal.



Accordingly, the titanium is converted to an iodide (specifically, TiI_4), and the
5 iodide is subsequently decomposed at the heated substrate 104 to deposit titanium
material 110. The reactions described above are merely exemplary reactions, and it is to
be understood that the chemistry of metal transport in apparatus 100 can comprise other
reactions in addition to, or alternatively to, those described.

A rate of transfer of a material from feedstock 106 to product 110 can depend on,
10 among other things, a temperature differential between feedstock 106 and substrate 104,
a concentration of iodine, and kinetics of reaction of a particular metal with iodine to
form an iodide, as well as kinetics of reaction of a particular metal iodide to decompose
to form the metallic element. Accordingly, if feedstock 106 comprises a mixture of
elements, the product 110 can comprise a mixture having a different stoichiometry than
15 that initially present as feedstock 106 due to, for example, differences in kinetics of
iodide formation of various metallic iodides, and/or differences in kinetics of iodide
decomposition of various metallic iodides.

Feedstock 106 can comprise predominately zirconium, and can further comprise
one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co,
20 Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W,
Y, and Yb. Alternatively, feedstock 106 can comprise predominately titanium, and can
further comprise one or more elements selected from the group consisting of Al, B, Ba,
Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr,
Ta, V, W, Y, Yb and Zr. Also, product 110 can comprise predominately zirconium, and
25 can further comprise one or more elements selected from the group consisting of Al, B,
Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc,
Sm, Sr, Ta, Ti, V, W, Y, and Yb. Alternatively, product 110 can comprise
predominately titanium, and can further comprise one or more elements selected from

the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr.

Fig. 6 is a block diagram description of a system which can be utilized for the processing of step 18 of Fig. 1. Specifically, Fig. 6 illustrates a system 150 comprising a feed port 154, a cooled hearth 156, and a mold 158. In operation, a feed material is poured through port 154 and melted by vacuum melting (such as, for example, with an electron beam gun) to form a homogeneous molten mixture of the elements present in the feed material. The molten mixture is subsequently poured into cooled hearth 156, and then flowed into a mold 158. Mold 158 can be in the form of, for example, an ingot can. Accordingly, the material flowed into mold 158 can cool to form an ingot. The ingot will preferably have a homogeneous composition of the elements initially present in the feed material.

The feed material provided to apparatus 150 can be a product of either the reduction process of step 12 of Fig. 1, the electrolysis process of step 14 of Fig. 1, or the iodide process of step 16 of Fig. 1. Regardless, the feedstock will preferably comprise a mixture of metals, such as, for example, a titanium-based material having at least 0.001% of non-titanium metals; or a zirconium-based material having at least 0.001% of non-zirconium metals. If the feed material is titanium-based, the non-titanium metal content of the ingot can be in a range of from 0.001% to 50%, such as, for example, a range of from 0.001% to 10%. The non-titanium content can be, for example, at least 0.01%, and in particular embodiments can be at least 0.1%. Alternatively, if the material formed in the ingot is zirconium-based, the non-zirconium metal content can be in the range of from 0.001% to 50%, such as, for example, from 0.001% to 10%. Further, the non-zirconium content can be at least 0.01%, and in particular embodiments can be at least 0.1%.

A cooled ingot formed by the process of Fig. 6 can be utilized for forming a sputtering target. Sputtering targets comprising a homogeneous mixture of metallic elements can be particularly useful in sputtering processes in which it is desired to form a titanium-based or zirconium-based barrier layer for preventing copper diffusion.

If the barrier layer is to be a titanium-based material, such barrier layer can be formed by sputter-deposition from a target comprising, for example, titanium in combination with one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr. It is noted that many of the elements utilized in a sputtering target of the present invention are elements which are typically precluded from titanium-based sputtering targets of the prior art. Accordingly, there has not been a process developed in the prior art for forming a homogeneous mixture of titanium with one or more of the listed elements. However, for sputtering applications of the present invention it can be desired that a target comprise a homogeneous mixture throughout of all of the elements present in the sputtering target. Methodology of the present invention can enable such homogeneous mixture to be formed. Specifically, since methodology of the present invention melts a mixed-metal feedstock, methodology of the present invention can form a homogeneous mixed-metal ingot which can in turn be utilized to form a sputtering target with a homogeneous mixed-metal composition throughout.

If the barrier layer is to be a zirconium-based material, such barrier layer can be formed by sputter-deposition from a target comprising, for example, zirconium in combination with one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb. The zirconium can be present in the sputtering target to exemplary concentrations of at least 55%, at least 70%, at least 90%, at least 94%, or at least 97%. In particular applications, the amount of non-zirconium metals can be provided to a sufficient concentration within the sputtering target that the zirconium is present to less than 99% or less than 98%, while still being a majority element of the target. Accordingly, the target can comprise, for example, a concentration of zirconium in a range of from about 50% to about 98%, or can comprise a range of zirconium of from about 50% to about 99%. Further, the sputtering target can consist essentially of, or consist of, zirconium and titanium.

Zirconium-based sputtering targets of the type described herein can have properties similar to those of titanium-based sputtering targets, and accordingly can be used for forming diffusion barriers to impede or prevent copper diffusion from copper-containing materials to other components associated with semiconductor substrates.

- 5 There has not been a process developed in the prior art for forming a sputtering target consisting of a homogeneous mixture of zirconium with one or more of the listed elements, but methodology of the present invention can enable such homogeneous mixture to be formed. Specifically, since methodology of the present invention melts a mixed-metal feedstock, methodology of the present invention can form a homogeneous
10 mixed-metal zirconium-based ingot which can in turn be utilized to form a sputtering target with a homogeneous zirconium-based mixed-metal composition throughout.

- If the barrier layer is to be a titanium-based material, such barrier layer can be formed by sputter-deposition from a target comprising, consisting essentially of, or consisting of titanium and boron. The titanium can be present in the sputtering target to
15 exemplary concentrations of at least 70%, at least 90%, at least 94%, or at least 97%. In particular applications, the amount of boron can be provided to a sufficient concentration within the sputtering target that the boron is present to greater than 5 ppm in a target pure to 5N5, greater 50 ppm in a target pure to 4N5, greater than 500 ppm in a target pure to 3N5, or greater than one part per thousand in a target pure to 3N. Titanium/boron
20 mixed-metal sputtering targets can be used for forming diffusion barriers to impede or prevent copper diffusion from copper-containing materials to other components associated with semiconductor substrates. There has not been a process developed in the prior art for forming a sputtering target consisting of a homogeneous mixture of titanium with boron, but methodology of the present invention can enable such homogeneous
25 mixture to be formed. Specifically, since methodology of the present invention melts a mixed-metal feedstock, methodology of the present invention can form a homogeneous mixed-metal titanium/boron ingot which can in turn be utilized to form a sputtering target with a homogeneous titanium and boron mixed-metal composition throughout.

CLAIMS

1. A method of forming a titanium-based mixed-metal product, comprising combining a mixture of titanium halide and at least one metal halide with a reducing agent to produce a mixed-metal product comprising titanium and at least one metal
5 corresponding to the at least one metal of the at least one metal halide; wherein,

the at least one metal of the at least one metal halide is selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr;

the mixed-metal product is at least 99.95% pure; and

- 10 the mixed-metal product comprises greater than 0.05% of the at least one metal.

2. The method of claim 1 wherein the mixed-metal product comprises greater than 0.1% of the at least one metal.

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3. The method of claim 1 wherein the mixed-metal product comprises greater than 0.5% of the at least one metal.

4. The method of claim 1 wherein the at least one metal is only one metal.

20

5. The method of claim 1 wherein the at least one metal is two metals.

6. The method of claim 1 wherein the at least one metal comprises Zr.

- 25 7. The method of claim 1 wherein the at least one metal comprises Hf.

8. A method of forming a titanium-based mixed-metal product, comprising electrolytically depositing a mixed-metal product comprising a mixture of titanium and at least one other metal, the at least one other metal being selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr; wherein
- 5 the mixed-metal product is at least 99.95% pure; and
- the mixed-metal product comprises greater than 0.05% of the at least one other metal.
- 10 9. The method of claim 8 wherein the mixed-metal product comprises greater than 0.1% of the at least one other metal.
10. The method of claim 8 wherein the mixed-metal product comprises greater than 0.5% of the at least one other metal.
- 15 11. The method of claim 8 wherein the at least one other metal is only one other metal.
12. The method of claim 8 wherein the at least one other metal is two other metals.
- 20 13. The method of claim 8 wherein the at least one metal comprises Zr.
14. The method of claim 8 wherein the at least one metal comprises Hf.

15. A method of forming a titanium-based mixed-metal product, comprising:

providing a mixture of titanium and least one other metal in a reaction apparatus with iodine gas and a heated substrate; the at least one other metal being selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr;

reacting the titanium and the at least one other metal with the iodine gas to form titanium iodide and an iodide of the at least one other metal;

transferring the titanium iodide and the iodide of the at least one other metal to the heated substrate, and utilizing heat from the substrate to decompose the iodides and produce a mixed-metal product comprising titanium and the at least one other metal; wherein

the mixed-metal product is at least 99.95% pure; and

the mixed-metal product comprises greater than 0.05% of the at least one other metal.

16. The method of claim 15 wherein the mixed-metal product comprises greater than 0.1% of the at least one other metal.

17. The method of claim 15 wherein the mixed-metal product comprises greater than 0.5% of the at least one other metal.

18. The method of claim 15 wherein the at least one other metal is only one other metal.

19. The method of claim 15 wherein the at least one other metal is two other metals.

20. The method of claim 15 wherein the at least one metal comprises Zr.

21. The method of claim 15 wherein the at least one metal comprises Hf.
22. A method of forming a zirconium-based mixed-metal product, comprising combining a mixture of zirconium halide and at least one metal halide with a reducing agent to produce a mixed-metal product comprising zirconium and at least one metal corresponding to the at least one metal of the at least one metal halide; wherein,
the at least one metal of the at least one metal halide is selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb;
the mixed-metal product is at least 99.95% pure; and
the mixed-metal product comprises greater than 0.05% of the at least one metal.
23. The method of claim 22 wherein the mixed-metal product comprises greater than 0.1% of the at least one metal.
24. The method of claim 22 wherein the mixed-metal product comprises greater than 0.5% of the at least one metal.
25. The method of claim 22 wherein the at least one metal is only one metal.
26. The method of claim 22 wherein the at least one metal is two metals.
27. The method of claim 22 wherein the at least one metal comprises Ti.
28. The method of claim 22 wherein the at least one metal comprises Hf.

29. A method of forming a zirconium-based mixed-metal product, comprising electrolytically depositing a mixed-metal product comprising a mixture of zirconium and at least one other metal, the at least one other metal being selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb; wherein

the mixed-metal product is at least 99.95% pure; and

the mixed-metal product comprises greater than 0.05% of the at least one other metal.

30. The method of claim 29 wherein the mixed-metal product comprises greater than 0.1% of the at least one other metal.

31. The method of claim 29 wherein the mixed-metal product comprises greater than 0.5% of the at least one other metal.

32. The method of claim 29 wherein the at least one other metal is only one other metal.

33. The method of claim 29 wherein the at least one other metal is two other metals.

34. The method of claim 29 wherein the at least one metal comprises Ti.

35. The method of claim 29 wherein the at least one metal comprises Hf.

36. A method of forming a zirconium-based mixed-metal product, comprising:
providing a mixture of zirconium and least one other metal in a reaction
apparatus with iodine gas and a heated substrate; the at least one other metal
being selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy,
5 Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W,
Y, and Yb;

reacting the zirconium and the at least one other metal with the iodine gas
to form zirconium iodide and an iodide of the at least one other metal;

10 transferring the zirconium iodide and the iodide of the at least one other
metal to the heated substrate, and utilizing heat from the substrate to decompose
the iodides and produce a mixed-metal product comprising zirconium and the at
least one other metal; wherein

the mixed-metal product is at least 99.95% pure; and

15 the mixed-metal product comprises greater than 0.05% of the at least one
other metal.

37. The method of claim 36 wherein the mixed-metal product comprises greater
than 0.1% of the at least one other metal.

20 38. The method of claim 36 wherein the mixed-metal product comprises greater
than 0.5% of the at least one other metal.

39. The method of claim 36 wherein the at least one other metal is only one other
metal.

25

40. The method of claim 36 wherein the at least one other metal is two other metals.

41. The method of claim 36 wherein the at least one metal comprises Ti.

42. The method of claim 36 wherein the at least one metal comprises Hf.
43. A method of forming a titanium-based mixed-metal ingot, comprising:
combining a mixture of titanium halide and one or more other metal halides
5 with a reducing agent to produce a mixed-metal product; wherein the one or
more other metal halides are selected from the group consisting of halides of Al,
B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd,
Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr;
melting the mixed-metal product to form a molten mixed-metal material;
10 and
cooling the molten mixed-metal material into a mixed-metal ingot; the
ingot comprising titanium and one or more other metals; the one or more other
metals corresponding to one or more of the other metals of the one or more
metal halides; the titanium being the majority element of the ingot; the ingot
15 having a purity of titanium and the one or more other metals of at least 99.95%.
44. The method of claim 43 wherein the titanium halide is a titanium chloride, and
wherein the other metal halides are metal chlorides.
- 20 45. The method of claim 43 wherein the ingot has a purity of the titanium and the
one or more other metals of at least 99.995%.
46. The method of claim 43 wherein the ingot has a purity of the titanium and the
one or more other metals of at least 99.9995%.
- 25 47. The method of claim 43 wherein the one or more other metals comprise
zirconium.

48. The method of claim 43 wherein the one or more other metals is only one other metal and consists of zirconium.

49. The method of claim 43 further comprising forming a sputtering target from the ingot.

50. A method of forming a zirconium-based mixed-metal ingot, comprising:
combining a mixture of zirconium halide and one or more other metal halides with a reducing agent to produce a mixed-metal product;
melting the mixed-metal product to form a molten mixed-metal material;
and
cooling the molten mixed-metal material into a mixed-metal ingot, the ingot comprising zirconium and one or more other metals corresponding to the one or more other metals of the one or more metal halides, the zirconium being the majority element of the ingot; the ingot having a purity of zirconium and the one or more other metals of at least 99.95%.

51. The method of claim 50 wherein the zirconium halide is a zirconium chloride, and wherein the other metal halides are metal chlorides.

52. The method of claim 50 wherein the ingot has a purity of the zirconium and the one or more other metals of at least 99.995%.

53. The method of claim 50 wherein the ingot has a purity of the zirconium and the one or more other metals of at least 99.9995%.

54. The method of claim 50 wherein the one or more other metals are selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb.

55. The method of claim 50 wherein the one or more other metals comprise titanium.

5 56. The method of claim 50 wherein the one or more other metals is only one other metal and consists of titanium.

57. The method of claim 50 wherein the reducing agent is selected from the group consisting of sodium metal and magnesium metal.

10

58. The method of claim 50 further comprising forming a sputtering target from the ingot.

59. A method of forming a titanium-based mixed-metal ingot, comprising:

15

electrolytically depositing a mixture of titanium and at least one other metal, the deposited mixture being a mixed-metal product;

melting the mixed-metal product to form a molten mixed-metal material;

and

cooling the molten mixed-metal material into a mixed-metal ingot, the ingot comprising the titanium and the at least one other metal, the titanium

20

being the majority element of the ingot; the ingot having a purity of titanium and the at least one other metal of at least 99.95%.

60. The method of claim 59 wherein the at least one other metal that is deposited

25 has a deposition reduction potential within ± 0.7 volts of the reduction potential for conversion of Ti^{2+} to elemental Ti.

61. The method of claim 59 wherein the at least one other metal that is deposited has a deposition reduction potential within ± 0.5 volts of the reduction potential for conversion of Ti^{2+} to elemental Ti.

5 62. The method of claim 59 wherein the at least one other metal that is deposited includes Zr.

63. The method of claim 59 wherein the at least one other metal that is deposited is only one other metal and consists of Zr.

10

64. The method of claim 59 further comprising:

combining a mixture of titanium halide and metal halide with a reducing agent to produce a mixed-metal feedstock, the metal halide comprising the at least one other metal; and

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wherein the electrolytically depositing utilizes the mixed-metal feedstock as an anode and comprises transferring titanium and the at least one other metal from the anode to a cathode whereupon the titanium and at least one other metal are deposited as the mixed-metal product.

20

65. A method of forming a zirconium-based mixed-metal ingot, comprising:

electrolytically depositing a mixture of zirconium and at least one other metal, the deposited mixture being a mixed-metal product;

melting the mixed-metal product to form a molten mixed-metal material; and

25

cooling the molten mixed-metal material into a mixed-metal ingot, the ingot comprising the zirconium and the at least one other metal, the zirconium being the majority element of the ingot; the ingot having a purity of zirconium and the at least one other metal of at least 99.95%.

66. The method of claim 65 wherein the at least one other metal that is deposited has a deposition reduction potential within ± 0.7 volts of the reduction potential for conversion of Zr^{2+} to elemental Zr.

5 67. The method of claim 65 wherein the at least one other metal that is deposited has a deposition reduction potential within ± 0.5 volts of the reduction potential for conversion of Zr^{2+} to elemental Zr.

68. The method of claim 65 wherein the at least one other metal that is deposited
10 includes Ti.

69. The method of claim 65 wherein the at least one other metal that is deposited is only one other metal and consists of Ti.

15 70. The method of claim 65 further comprising:
combining a mixture of zirconium halide and metal halide with a reducing agent to produce a mixed-metal feedstock, the metal halide comprising the at least one other metal; and
wherein the electrolytically depositing utilizes the mixed-metal feedstock
20 as an anode and comprises transferring zirconium and the at least one other metal from the anode to a cathode whereupon the zirconium and at least one other metal are deposited as the mixed-metal product.

71. A method of forming a titanium-based mixed-metal ingot, comprising:
- providing a mixture of titanium and least one other metal in a reaction apparatus with iodine gas and a heated substrate;
- reacting the titanium and the at least one other metal with the iodine gas to form titanium iodide and an iodide of the at least one other metal;
- transferring the titanium iodide and the iodide of the at least one other metal to the heated substrate, and utilizing heat from the substrate to decompose the iodides and produce a mixed-metal product, the mixed-metal product comprising titanium and the at least one other metal;
- melting the mixed-metal product to form a molten mixed-metal material; and
- cooling the molten mixed-metal material into a mixed-metal ingot, the ingot comprising the titanium and the at least one other metal, the titanium being the majority element of the ingot; the ingot having a purity of titanium and the at least one other metal of at least 99.95%.

72. The method of claim 71 wherein the at least one other metal is selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, Yb and Zr.

73. The method of claim 71 wherein the at least one other metal comprises zirconium.

74. The method of claim 71 wherein the at least one other metal is only one other metal and consists of zirconium.

75. The method of claim 71 further comprising forming the mixture of titanium and the at least one other metal by combining a mixture of titanium halide and metal halide with a reducing agent to produce the mixture, the metal halide comprising the at least one other metal.

5

76. The method of claim 71 further comprising forming the mixture of titanium and the at least one other metal by electrolytically depositing the mixture of titanium and the at least one other metal.

10 77. The method of claim 76 further comprising:

combining a mixture of titanium halide and metal halide with a reducing agent to produce a mixed-metal feedstock, the metal halide comprising the at least one other metal; and

15 wherein the electrolytically depositing utilizes the mixed-metal feedstock as an anode and comprises transferring titanium and the at least one other metal from the anode to a cathode whereupon the titanium and at least one other metal are deposited as the mixture of titanium and the at least one other metal.

78. A method of forming a zirconium-based mixed-metal ingot, comprising:
providing a mixture of zirconium and least one other metal in a reaction
apparatus with iodine gas and a heated substrate;
reacting the zirconium and the at least one other metal with the iodine gas
to form zirconium iodide and an iodide of the at least one other metal;
transferring the zirconium iodide and the iodide of the at least one other
metal to the heated substrate, and utilizing heat from the substrate to decompose
the iodides and produce a mixed-metal product, the mixed-metal product
comprising zirconium and the at least one other metal;
melting the mixed-metal product to form a molten mixed-metal material;
and
cooling the molten mixed-metal material into a mixed-metal ingot, the
ingot comprising the zirconium and the at least one other metal, the zirconium
being the majority element of the ingot; the ingot having a purity of zirconium
and the at least one other metal of at least 99.95%.

79. The method of claim 78 wherein the at least one other metal is selected from the
group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg,
Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb.

80. The method of claim 78 wherein the at least one other metal comprises titanium.

81. The method of claim 78 wherein the at least one other metal is only one other
metal and consists of titanium.

82. The method of claim 78 further comprising forming the mixture of zirconium and the at least one other metal by combining a mixture of zirconium halide and metal halide with a reducing agent to produce the mixture, the metal halide comprising the at least one other metal.

5

83. The method of claim 78 further comprising forming the mixture of zirconium and the at least one other metal by electrolytically depositing the mixture of zirconium and the at least one other metal.

10 84. The method of claim 83 further comprising:

combining a mixture of zirconium halide and metal halide with a reducing agent to produce a mixed-metal feedstock, the metal halide comprising the at least one other metal; and

wherein the electrolytically depositing utilizes the mixed-metal feedstock as an anode and comprises transferring zirconium and the at least one other metal from the anode to a cathode whereupon the zirconium and at least one other metal are deposited as the mixture of zirconium and the at least one other metal.

15

20 85. A sputtering target comprising Zr and one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, V, W, Y, and Yb; the Zr being the majority element of the target.

25 86. The sputtering target of claim 85 wherein the Zr concentration within the target is at least 70%.

87. The sputtering target of claim 85 wherein the Zr concentration within the target is at least 90%.

5 88. The sputtering target of claim 85 wherein the Zr concentration within the target is at least 94%.

89. The sputtering target of claim 85 wherein the Zr concentration within the target is at least 97%.

10 90. The sputtering target of claim 85 wherein the Zr concentration within the target is less than 98%.

91. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is in a range of from 0.001% to 50% of the ingot.

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92. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is in a range of 0.001% to 10% of the ingot.

20 93. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is at least 0.01% of the ingot.

94. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is at least 0.1% of the ingot.

25 95. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is at least 1% of the ingot.

96. The sputtering target of claim 85 wherein the total non-zirconium metal content of the target is at least 2% of the ingot.

97. The sputtering target of claim 85 consisting of Zr and Ti.

98. A sputtering target comprising Zr and Ti; the Zr being the majority element of
5 the target and being present to a concentration within the target of at least 55%.

99. The sputtering target of claim 98 wherein the Zr concentration within the target
is at least 70%.

10 100. The sputtering target of claim 98 wherein the Zr concentration within the target
is at least 90%.

101. The sputtering target of claim 98 wherein the Zr concentration within the target
is at least 94%.

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102. The sputtering target of claim 98 wherein the Zr concentration within the target
is at least 97%.

103. The sputtering target of claim 98 wherein the Zr concentration within the target
20 is less than 98%.

104. A sputtering target comprising Ti and B; the Ti being the majority element of
the target.

25 105. The sputtering target of claim 104 wherein the Ti concentration within the target
is at least 70%.

106. The sputtering target of claim 104 wherein the Ti concentration within the target is at least 90%.

107. The sputtering target of claim 104 wherein the Ti concentration within the target
5 is at least 94%.

108. The sputtering target of claim 104 wherein the Ti concentration within the target is at least 97%.

10 109. The sputtering target of claim 108 wherein the B content of the target is greater than 5 ppm.

110. The sputtering target of claim 108 wherein the B content of the target is greater than 50 ppm.

15 111. The sputtering target of claim 108 wherein the B content of the target is greater than 500 ppm.

112. The sputtering target of claim 108 wherein the B content of the target is greater
20 than one part per thousand.

113. The sputtering target of claim 104 wherein the Ti concentration within the target is less than 98%.

25 114. The sputtering target of claim 104 wherein the B content of the target is greater than 5 ppm.

115. The sputtering target of claim 104 wherein the B content of the target is greater than 50 ppm.

116. The sputtering target of claim 104 wherein the B content of the target is greater than 500 ppm.
- 5 117. The sputtering target of claim 104 wherein the B content of the target is greater than one part per thousand.
118. The sputtering target of claim 104 consisting of Ti and B.

ABSTRACT OF THE DISCLOSURE

The invention encompasses methods of forming titanium-based mixed-metal materials and zirconium-based mixed-metal materials utilizing one or more of a reduction process, electrolysis process and iodide process. The invention also
5 encompasses a sputtering target comprising zirconium and one or more elements selected from the group consisting of Al, B, Ba, Be, Ca, Ce, Co, Cs, Dy, Er, Fe, Gd, Hf, Ho, La, Mg, Mn, Mo, Nb, Nd, Ni, Pr, Sc, Sm, Sr, Ta, Ti, V, W, Y, and Yb. The invention also encompasses a sputtering target comprising titanium and boron.

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APPLICATION FOR LETTERS PATENT

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**Sputtering Target Compositions, and Methods of
Inhibiting Copper Diffusion into a Substrate**

* * * * *

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Sputtering Target Compositions, and Methods of Inhibiting Copper Diffusion into a Substrate

TECHNICAL FIELD

The invention pertains to titanium alloy thin films with improved copper diffusion barrier properties. The invention also pertains to titanium alloy sputtering targets, and additionally pertains to methods of inhibiting copper diffusion into substrates.

BACKGROUND OF THE INVENTION

10 Integrated circuit interconnect technology is changing from aluminum subtractive processes to copper dual damascene processes. The shift from aluminum to copper is causing new barrier layer materials to be developed. Specifically, titanium nitride (TiN) films had been utilized as barrier layers in the aluminum technologies to inhibit aluminum atoms from diffusing into adjacent dielectric materials and causing device failure. The TiN films could be formed by, for example, reactively sputtering a titanium target in a nitrogen atmosphere. The TiN films are found to be poor barrier layers relative to copper because the diffusivity of copper atoms through TiN films is too high.

 The problems associated with TiN barrier layers are described with reference to
20 Figs. 1 and 2. Specifically, Fig. 1 illustrates a preferred barrier layer construction, and Fig. 2 illustrates problems associated with TiN barrier layers.

 Referring initially to Fig. 1, a semiconductor wafer fragment 10 is illustrated. Wafer fragment 10 comprises a substrate 12 which can comprise, for example, monocrystalline silicon. To aid in interpretation of the claims that follow, the terms "semiconductive substrate" and "semiconductor substrate" are defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in

assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

An insulative layer 14 is formed over substrate 12. Insulative layer 14 can comprise, for example, silicon dioxide or borophosphous silicate glass (BPSG). Alternatively, layer 14 can comprise a so-called "low-k" dielectric material.

A barrier layer 16 is formed to extend within a trench in insulative material 14, and a copper seed layer 18 is formed on barrier layer 16. Copper seed layer 18 can be
10 formed by, for example, sputter deposition from a high purity copper target, with the term "high purity" referring to a target having at least 99.995% purity (i.e., 4N5 purity). A copper material 20 is formed over copper seed layer 18, and can be formed by, for example, electrochemical deposition onto seed layer 18.

Barrier layer 16 is provided to prevent copper diffusion from materials 18 and 20 into insulative material 14. It is found that prior art titanium materials are not suitable as barrier layers for preventing diffusion of copper. Specifically, it is found that neither TiN or pure Ti works well to prevent copper diffusion. Problems associated with prior art titanium-comprising materials are described with reference to Fig. 2, which shows the construction 10 of Fig. 1, but which is modified to illustrate specific problems that can
20 occur if either pure titanium or titanium nitride are utilized as barrier layer 16.

Specifically, Fig. 2 shows channels 22 extending through barrier layer 16. Channels 22 can result from columnar grain growth associated with the titanium materials of barrier layer 16. Channels 22 effectively provide paths for copper diffusion through a titanium-comprising barrier layer 16 and into insulative material 14. The columnar grain growth can occur during formation of a Ti or TiN layer 16, or during high temperature processing subsequent to the deposition. Specifically, it is found that even when prior art

titanium materials are deposited without columnar grain problems, the materials are not chemically stable to temperatures in excess of 450°C and columnar grains will result when the materials are exposed to such temperatures. Accordingly, copper diffusion can occur through prior art titanium and titanium nitride materials exposed to temperatures of less than 500°C.

Another problem that can occur in attempting to utilize prior art titanium materials as barrier layers can occur in attempting to adhere the titanium materials to the dielectric material 14. Specifically, it is often found that titanium materials adhere poorly to commonly-used dielectric materials (such as, for example, silicon dioxide), and that
10 circuit defects can be caused by such poor adhesion.

In an effort to avoid the problems described with reference to Fig. 2, there has been a development of non-titanium barrier materials for diffusion layer 16. Among the materials which have been developed is tantalum nitride (TaN). It is found that TaN can have a close to nanometer-sized grain structure and good chemical stability as a barrier layer for preventing copper diffusion. However, a difficulty associated with TaN is that the high cost of tantalum can make it difficult to economically incorporate TaN layers into semiconductor fabrication processes.

Titanium can be a lower cost material than tantalum. Accordingly, it could be possible to reduce materials cost for the microelectronics industry relative to utilization of
20 copper interconnect technology if methodology could be developed for utilizing titanium-comprising materials, instead of tantalum-comprising materials, as barrier layers for inhibiting copper diffusion. It is therefore desirable to develop new titanium-containing materials which are suitable as barrier layers for impeding or preventing copper diffusion.

SUMMARY OF THE INVENTION

The invention described herein relates to new titanium-comprising materials which can be utilized for forming titanium alloy sputtering targets. The titanium alloy sputtering targets can be reactively sputtered in a nitrogen atmosphere to form an alloy TiN film, or alternatively in a nitrogen and oxygen atmosphere to form an alloy TiON thin film. The thin films formed in accordance with the present invention can have a non-columnar grain structure, low electrical resistivity, high chemical stability, and barrier layer properties comparable to those of TaN. Further, the titanium alloy sputtering target materials produced in accordance with the present invention can be more cost-effective for semiconductor applications than are high-purity tantalum materials.

In one aspect, the invention encompasses a sputtering target comprising Ti and one or more elements which have a standard electrode potential of less than -1.0 volt.

In another aspect, the invention encompasses a method of inhibiting copper diffusion into a substrate. A first layer comprising titanium and one or more elements which have a standard electrode potential of less than -1.0V is formed over the substrate. A copper-containing layer is then formed over the first layer and separated from the substrate by the first layer. The first layer inhibits copper diffusion from the copper-containing layer to the substrate.

In yet another aspect, the invention encompasses a sputtering target comprising Ti and one or more elements which have melting temperatures greater than or equal to 2500°C, and wherein the one or more elements do not react with copper at temperatures of less than or equal to the melting temperatures of the elements.

In yet another aspect, the invention encompasses a sputtering target comprising Ti and one or more elements which differences in atomic radii relative to Ti of at least 10%, and in some applications at least 20%.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic, cross-sectional view of a prior art semiconductor wafer fragment illustrating a conductive copper material separated from an insulative material by a barrier layer.

Fig. 2 is a view of the Fig. 1 prior art wafer fragment illustrating problems which can occur when utilizing prior art Ti-containing materials as the barrier layer.

Fig. 3 is a diagrammatic, cross-sectional view of a semiconductor wafer fragment
10 at a preliminary step of a method of the present invention.

Fig. 4 is a view of the Fig. 3 wafer fragment shown at a processing step subsequent to that of Fig. 4.

Fig. 5 is a view of the Fig. 3 wafer fragment shown at a processing step subsequent to that of Fig. 4.

Fig. 6 is a view of the Fig. 3 wafer fragment shown at a processing step subsequent to that of Fig. 5.

Fig. 7 is an expanded view of a portion of the Fig. 5 wafer fragment.

Fig. 8 is a diagrammatic graph illustrating a relative concentration of a material "Q" relative to a copper layer, TiQ layer and SiO layer along an axis shown in Fig. 4.

20 Fig. 9 is a diagrammatic graph of a relative concentration of a material "Q" relative to a copper layer, TiQ layer and SiO layer along an axis shown in Fig. 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Exemplary embodiments of the present invention are described with reference to Figs. 3-9. Referring initially to Fig. 3, a semiconductor wafer fragment 50 is illustrated. Wafer fragment 50 comprises a semiconductive material substrate 52, such as, for

example, monocrystalline silicon. An insulative material 54 is formed over substrate 52, and an opening 56 is formed into insulative material 54. Materials 52 and 54 can comprise the same materials as described with reference to the prior art for materials 12 and 14, respectively. Opening 56 can comprise, for example, a trench for formation of copper in a dual damascene process.

Referring to Fig. 4, a barrier layer 58 is formed over insulative layer 54 and within opening 56. In accordance with the present invention, barrier layer 58 comprises titanium, and is configured to impede diffusion from subsequently-formed copper layers into insulative material 54. In one aspect of the invention, barrier layer 58 comprises titanium and one or more elements which have a standard electrode potential (specifically, a standard reduction potential) of less than -1.0V (i.e. less than -1.0 volt). Suitable elements can be selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Y, Mn, V and Zr. Further, barrier layer 58 can consist essentially of the titanium and one or more elements having a standard electrode potential of less than about -1.0V, or can consist of the titanium and one or more elements having a standard electrode potential of less than -1.0V. Barrier layer 58 can also comprise one or both of nitrogen and oxygen in addition to the Ti and the one or more elements having a standard electrode potential of less than -1.0V. Layer 58 can be considered as a film formed over substrate 54, and in particular embodiments will have a thickness of from about 5 nanometers to about 50 nanometers, and can specifically have a thickness of from about 5 nanometers to about 20 nanometers.

In another aspect of the invention, barrier layer 58 comprises titanium and one or more elements which have a melting temperature of greater than or equal to about 2500°C, and no reaction with copper at temperatures equal to or below the melting temperature. Suitable elements can be selected from the group consisting of Mo, Ta and W. Further, barrier layer 58 can consist essentially of the titanium and one or more

elements having a melting temperature of greater than or equal to about 2500°C, or can consist of the titanium and one or more elements having a melting temperature of greater than or equal to about 2500°C. Barrier layer 58 can also comprise one or both of nitrogen and oxygen in addition to the Ti and the one or more elements having a melting temperature of greater than or equal to about 2500°C. Layer 58 can be considered as a film formed over substrate 54, and in particular embodiments will have a thickness of from about 5 nanometers to about 50 nanometers, and can specifically have a thickness of from about 5 nanometers to about 20 nanometers. The elements having a melting temperature of greater than or equal to about 2500°C can stabilize a titanium alloy due to refractory characteristics of the elements.

One aspect of the materials of the present invention that can be important in maintaining desired small grain sizes in barrier layers and sputtering targets of the present invention is that the elements incorporated into the titanium-containing targets can have atomic sizes which are more than 10% different than the atomic size of titanium, and preferably more than 20% different than the atomic size of titanium. Such difference in atomic size can disrupt a titanium lattice structure, and accordingly impede grain growth within the lattice. A magnitude of difference in grain size between the titanium and the other elements incorporated into barrier layer 58 can effect the amount by which a lattice is disrupted, and accordingly can influence an amount of grain growth occurring at various temperatures. It can therefore be preferable to utilize elements having larger differences in size relative to titanium than atoms having less difference in size relative to titanium. A group of elements having an atomic radii difference relative to titanium of at least 10% is Si, P, S, Sc, C Mn, Fe, Co, Ni, Y, and In; and a group of elements having an atomic radii difference relative to titanium of at least 20% is Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb. It is noted that some of the elements having an atomic radii difference relative to titanium of greater than 10%, or greater than 20%, overlap

with the elements having a standard electrode potential of less than -1.0V, and some do not. The present invention encompasses utilizing elements having an atomic radii difference relative to titanium of greater than 10% (or in some applications greater than 20%) in combination with titanium for forming barrier layers, and accordingly comprises sputtering targets comprising titanium and one or more of Si, P, S, Sc, C Mn, Fe, Co, Ni, Y, In, Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb. The concentration of materials other than titanium in such targets can be less than 6 atomic percent, and can, for example, be less than 3 atomic percent or less than 2 atomic percent. In exemplary applications in which Be is utilized in a target composition with Ti, an E-beam melt
10 method can be incorporated into methodology for forming an alloy of Ti and Be.

In an exemplary process, layer 58 is a barrier layer for preventing diffusion from a conductive copper-containing material to insulative material 54. In such embodiment, it can be preferred that barrier layer 58 be conductive to provide additional electron flow beyond that provided by the conductive copper layer. In such embodiments, it can be preferred that barrier layer 58 have an electrical resistivity of equal to or less than $200\mu\Omega\cdot\text{cm}$.

An exemplary method of forming barrier layer 58 is to sputter deposit layer 58 from a target comprising titanium and one or more elements. The one or more elements can have a standard electrode potential of less than about -1.0V, an atomic radii size
20 difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to 2500°C. In particular embodiments, the target can consist essentially of the titanium and the one or more elements which have a standard electrode potential of less than about -1.0V, an atomic radii size difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to 2500°C. Also, the invention encompasses embodiments wherein the target consists of the titanium and the one or more elements having a standard electrode potential of less than about -1.0V, an atomic radii size

difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to 2500°C.

An exemplary target will comprise at least 90 atom% titanium, and from 0.001 atom% to 50 atom% of the one or more elements having a standard electrode potential of less than about -1.0V, an atomic radii size difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to 2500°C. In other embodiments, the target can comprise at least 99 atom% titanium, and from 0.001 atom% to 10 atom% of the one or more elements which have a standard electrode potential of less than -1.0V, an atomic radii size difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to 2500°C. In exemplary embodiments, the target comprises from 90 atom% to 99 atom% titanium, and the remainder of the target material is of zirconium, tantalum, yttrium, or magnesium.

Although previous targets have been produced having titanium and one or more of Al, Nb, Zr, Mn, V and Y; targets of the present invention can differ from the previous targets in that a concentration of the Al, Nb, Zr, Mn, V and Y can be smaller in targets of the present invention than in previous targets. Specifically, targets of the present invention can comprise less than 6 atom percent of elements other than titanium (i.e., can comprise greater than 94 atom percent titanium), in particular embodiments can comprise less than 3 atom percent of elements other than titanium (i.e., can comprise greater than 97 atom percent of titanium), and in further particular embodiments can comprise less than or equal to about 2 atom percent of atoms other than titanium (i.e., can comprise greater than or equal to 98 atom percent of titanium). For instance, a target of the present invention can consist of titanium and niobium, and comprise less than 12 weight percent (6.57 atom percent) of the niobium. An advantage of having a small concentration of materials other than titanium in targets of the present invention is that such can enable films sputtered from the targets to have properties (such as, for example, electrical

properties) more largely influenced by titanium than would films formed from targets having larger concentrations of materials other than titanium. Although targets having low concentrations of materials other than titanium can be preferred in methods of the present invention, it is to be understood that the invention is not limited to such targets except to the extent that such targets are recited in the claims which follow. Prior art titanium-comprising targets can be utilized for a new method in accordance with methodology of the present invention for forming copper barrier layers.

10 A target utilized in methodology of the present invention can be sputtered in an atmosphere such that only target materials are deposited in film 58, or alternatively can be sputtered in an atmosphere so that materials from the atmosphere are deposited in barrier layer 58 together with the materials from the target. For instance, the target can be sputtered in an atmosphere comprising a nitrogen-containing component to form a barrier layer 58 that comprises nitrogen in addition to the materials from the target. An exemplary nitrogen-containing component is diatomic nitrogen (N_2). The deposited thin film can be referred to by the stoichiometry $Ti_xQ_yN_z$, with "Q" being a label for the one or more elements having a standard electrode potential of less than $-1.0V$, an atomic radii size difference relative to Ti of at least 10%, and/or melting temperatures greater than or equal to $2500^{\circ}C$, that were incorporated into the target. In particular processing, the material $Ti_xQ_yN_z$ will comprise $x=0.3$ to 0.7 , $y=0.001$ to 0.1 , and $z=0.4$ to 0.6 ; and can
20 comprise $y=0.001$ to 0.01 .

Another exemplary method of forming barrier layer 58 is to sputter deposit the layer from a target comprising titanium and one or more elements other than titanium in the presence of both a nitrogen-comprising component and an oxygen-comprising component, to incorporate both nitrogen and oxygen into barrier layer 58. Such processing can form a barrier layer having the stoichiometry $Ti_xQ_yN_zO_w$, with Q again referring to the elements having an atomic radii size difference relative to Ti of at least

10%, elements comprising a standard electrode potential of less than about -1.0V, and/or elements having melting temperatures greater than or equal to 2500°C. The compound $Ti_xQ_yN_zO_w$ can comprise, for example, $x=0.3$ to 0.7 , $y=0.001$ to 0.1 , $z=0.4$ to 0.6 , and $w=0.0001$ to 0.0010 . The oxygen-containing component used to form the $Ti_xQ_yN_zO_w$, can be, for example O_2 .

There can be advantages to incorporating nitrogen and/or oxygen into a barrier layer 58, in that such incorporation can improve conductivity of the material of barrier layer 58 and/or can improve the high-temperature stability of the barrier layer relative to its ability to exclude copper diffusion at high temperatures. The nitrogen and/or oxygen can, for example, disturb a Ti columnar grain structure and thus form a more equi-axed grain structure.

Particular methodology for forming sputtering targets in accordance with the present invention and for depositing thin films from the sputtering targets are described below with reference to examples 1-4.

A barrier layer 58 formed in accordance with the present invention can comprise a grain size of less than or equal to 500 nanometers, and in particular processing can comprise a grain size of less than or equal to 100 nanometers. Further, the barrier layer material can have sufficient stability so that the grain size remains less than or equal to 500 nanometers, and in particular embodiments less than or equal to 100 nanometers, after the film is exposed to 500°C for 30 minutes in a vacuum anneal.

The small grain size of the film 58 of the present invention can enable the film to better preclude copper diffusion than can prior art titanium-containing films. Specifically, the prior art titanium-containing films frequently would form large grain sizes at processing above 450°C, and accordingly would have the columnar-type defects described above with reference to Fig. 2. Processing of the present invention can avoid

formation of such defects, and accordingly can enable better titanium-containing diffusion layers to be formed than could be formed by prior art processing.

Referring still to Fig. 4, a copper-containing seed layer 60 is formed over barrier layer 58. Copper-containing seed layer 60 can comprise, for example, high purity copper (i.e., copper which is at least 99.995% pure), and can be deposited by, for example, sputter deposition from a high purity copper target.

Fig. 5 illustrates wafer fragment 50 after it has been exposed to chemical-mechanical polishing to remove layers 58 and 60 from over an upper surface of insulative material 54 while leaving materials 58 and 60 within trench 56. Fig. 5 also illustrates processing that can occur specifically when elements having a standard electrode potential of less than -1.0V are in layer 58, and shows that layer 58 has been exposed to thermal processing causing diffusion of the elements having a standard electrode potential less than -1.0V to form a region 62 having a higher concentration of the elements than other regions of material 58. Suitable thermal processing which can cause such migration of the element having a standard electrode potential less than -1.0V includes an anneal at a temperature of about 500°C for a time of about 30 minutes, under vacuum.

Fig. 7 shows an expanded view of a region of the Fig. 5 wafer fragment 50, and more clearly illustrates the region 62. Fig. 7 also illustrates that another region 64 having an enhanced concentration of the elements with a standard electrode potential of less than -1.0V can be formed adjacent to copper-containing layer 60. Region 64 is not shown in Fig. 5 due to limitations of space in the drawing. It is to be understood that region 64 may be effectively eliminated in particular processing of the present invention, depending on the elements incorporated into barrier layer 58.

Figs. 8 and 9 graphically illustrate the aspect of the invention that elements with a standard electrode potential less than -1.0V can migrate within barrier layer 58 during a high-temperature anneal.

Referring first to Fig. 8, such illustrates a graph of a concentration of the elements with a standard electrode potential of less than -1.0V (illustrated as "Q", and specifically illustrated as a relative percent of "Q") relative to the copper of layer 60, the TiQ of layer 58 and the SiO of layer 54. It is noted that the TiQ and SiO are not intended to be stoichiometric representations of the materials of either barrier layer 58 or insulative material 54, but rather simply identify layers 58 and 64 in the drawing of Fig. 8. The
10 graph of Fig. 8 is illustrated along an axis shown in Fig. 4, and accordingly corresponds to a processing step prior to the anneal of Fig. 5.

Fig. 9 shows a graph similar to that of Fig. 8, but shows the graph along an axis of Fig. 5, and accordingly is showing relative concentrations after the Fig. 5 anneal. Fig. 9 illustrates that a concentration of Q is increased at an interface between the TiQ layer 58 and SiO layer 54, relative to a concentration throughout a middle region of TiQ. Fig. 9 also illustrates that a concentration of Q can be increased at an interface between copper-containing layer 60 and TiQ layer 58.

It is to be understood that even though Figs. 8 and 9 refer to insulative layer 54 specifically as a SiO layer, such is an exemplary composition for insulative layer 54, and
20 the invention encompasses embodiments wherein layer 54 comprises other insulative materials. It is also to be understood that the relative concentrations of Q shown in Fig. 9 are for illustrative purposes only, and that Fig. 9 is showing a qualitative representation of the concentrations of Q, rather than a quantitative representation.

An advantage of utilizing an element having a standard electrode potential of less than -1.0V is evidenced by Figs. 7, 8 and 9. Specifically, such element will tend to diffuse toward the interface regions of barrier layer 58 during an anneal. The element can

thus form the regions 62 and 64 of Fig. 7, which can have enhanced copper-barrier aspects relative to the remaining central region of layer 58. Also, the region 62 can have enhanced characteristics for adhering layer 58 to insulative material 54. Accordingly, barrier layers formed in accordance with the present invention can adhere to insulative materials better than barrier layers formed in accordance with the prior art, and can thus alleviate some of the problems associated with prior art barrier layers.

Fig. 6 illustrates wafer fragment 50 at a processing step subsequent to that of Fig. 5, and specifically shows a copper-containing material 70 formed within trench 56 (Fig. 5). Copper-containing material 70 can be formed by, for example, electrodeposition of copper onto seed layer 60. An advantage of having a conductive barrier layer 58 is evidenced in Fig. 6. Specifically, as trenches become increasingly smaller, the amount of the trench consumed by barrier layer 58 relative to that consumed by copper material 70 can increase. Accordingly, layers 58, 60 and 70 can be considered a conductive component, with layer 58 having an increasingly larger representative volume as trench sizes become smaller. A reason that layer 58 can have an increasingly larger volume is that there are limits relative to the thickness of layer 58 desired to maintain suitable copper-diffusion barrier characteristics. As the relative volume of layer 58 increases within the conductive component comprising layers 58, 60 and material 70, it can be desired to have good conductive characteristics within material 58 to retain good conductive characteristics within the conductive component.

EXAMPLES

The invention is illustrated by, but not limited to, the following examples.

EXAMPLE 1

10 A TiY target comprises 1.0at% Y, which is a reactive element with a standard electrode potential of -2.37V . A predetermined amount of 3N (99.9%) purity Y is added to a 5N (99.999%) purity Ti during a vacuum skull melt. After a homogeneous alloy is formed, the alloy is cast into a graphite mold to form a billet. The billet is forged and rolled using conventional thermomechanical processes and machined into a sputtering target. The TiY target is reactively sputtered in a N_2/Ar atmosphere, where N_2/Ar flow ratio is 0.4-0.6/1. The resulting TiY thin film has a composition of $\text{Ti}_x\text{Y}_y\text{N}_z$, with $x=0.3-0.7$, $y=0.001-0.01$, $z=0.3-0.6$. The thin film has a thickness of 5-50nm and an electrical resistivity below $200\mu\Omega\cdot\text{cm}$. The film has a nanometer sized grain structure, which is stable after a vacuum anneal at a temperature of at least about 500°C for a time of at least about 30 minutes. The film also has an improved adhesion to intermetal dielectrics and wetting characteristics by Cu. The thin film has overall properties that are adequate for a typical Cu/low-k dielectric process.

EXAMPLE 2

A TiY target comprises 1.0at% Y, which is a reactive element with a standard electrode potential of -2.37V . A predetermined amount of 3N purity Y is added to a 5N purity Ti during a vacuum skull melt. After a homogeneous alloy is formed, the alloy is cast into a graphite mold to form a billet. The billet is forged and rolled using conventional thermomechanical processes, and machined into a sputtering target. The target is reactively sputtered in a $\text{N}_2/\text{O}_2/\text{Ar}$ gas, with a $\text{N}_2/\text{O}_2/\text{Ar}$ ratio of 0.4-0.6/0.1-0.3/1. The resulting TiY thin film has a composition of $\text{Ti}_x\text{Y}_y\text{N}_z\text{O}_w$, with $x=0.3-0.7$, $y=0.001-0.01$, $z=0.3-0.6$, $w=0.0001-0.001$. The thin film has a thickness of 5-50nm and an electrical resistivity below $200\mu\Omega\cdot\text{cm}$. The film has an amorphous grain structure, which is stable after a vacuum anneal at a temperature of at least about 500°C for a time of at least about 30 minutes. The film also has an improved adhesion to intermetal dielectrics and wetting characteristics by Cu. The thin film has overall properties that are adequate for a typical Cu/low-k dielectric process.

EXAMPLE 3

A TiZr target comprises a specific amount of Zr, which is a reactive element with a standard electrode potential of -1.63V . A predetermined amount of Zr is added to Ti during a vacuum skull melt. After a homogenous alloy is formed, the alloy is cast into a graphite crucible to form a billet. The billet is forged and rolled using conventional thermomechanical processes and machined into a sputtering target. The TiZr target is reactively sputtered in a N_2/Ar or $\text{N}_2/\text{O}_2/\text{Ar}$ atmosphere. The resulting TiZr thin film has a thickness of 5-50 nm and an electrical resistivity below $200\mu\Omega\cdot\text{cm}$. The film has an amorphous grain structure, which is stable after 500°C and 30 minutes vacuum anneal.

- 10 The film also has an improved adhesion to intermetal dielectrics and wetting characteristics by Cu. The thin film has overall properties that are adequate for a typical Cu/low-k dielectric process.

EXAMPLE 4

- TiZr alloy sponge or crystal is directly melted in, for example, an electron beam furnace or a vacuum skull apparatus to form a homogenous TiZr ingot. The ingot is then forged and rolled using conventional thermomechanical processes and machined into a sputtering target. The TiZr target is reactively sputtered in a N_2/Ar or $\text{N}_2/\text{O}_2/\text{Ar}$ atmosphere. The resulting TiZr thin film has a thickness of 5-50 nm and an electrical resistivity below $200\mu\Omega\cdot\text{cm}$. The film has an amorphous grain structure, which is stable after 500°C and 30 minutes vacuum anneal. The film also has an improved adhesion to intermetal dielectrics and wetting characteristics by Cu. The thin film has overall properties that are adequate for a typical Cu/low-k dielectric process.
- 20

The embodiments described herein are exemplary embodiments, and it is to be understood that the invention encompasses embodiments beyond those specifically

described. For instance, the chemical-mechanical polishing described as occurring between the steps of Figs. 4 and 5, could instead be conducted after electrodeposition of the copper material 70 that is shown in Fig. 6. Also, the anneal described with reference to Fig. 5 as being utilized to form region 62 could be conducted instead after the processing of Fig. 6.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The
10 invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

CLAIMS

- 1 1. A sputtering target comprising Ti and one or more elements which have one or
2 both of a standard electrode potential of less than about -1.0V and a melting
3 temperature of at least 2500°C; the concentration of Ti being at least 94 atom percent
4 within the target.
- 1 2. The sputtering target of claim 1 wherein the one or more elements are selected
2 from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Mn,
3 V, Y, Mo, Ta, W and Zr.
- 1 3. A sputtering target comprising Ti and one or more elements selected from the
2 group consisting of Al, Ce, Cs, Hf, La, Nb, Nd, Sc, Mn, V, Y, Mo, Ta, W and Zr.
- 1 4. A sputtering target comprising Ti and less than 6 atom percent of one or more
2 elements having at least a 10 percent difference in atomic radii relative to titanium.
- 1 5. The sputtering target of claim 4 wherein the one or more elements are selected
2 from the group consisting of Si, P, S, Sc, Cr, Mn, Fe, Co, Ni, Y and In.
- 1 6. The sputtering target of claim 4 wherein the one or more elements have a
2 difference in atomic radii of at least 20% relative to Ti.
- 1 7. The sputtering target of claim 6 wherein the one or more elements are selected
2 from the group consisting of Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and
3 Yb.

- 1 8. The sputtering target of claim 6 wherein the one or more elements comprise C.
- 1 9. The sputtering target of claim 6 wherein the one or more elements comprise B.
- 1 10. A sputtering target comprising Ti and one or more elements which have a
2 standard electrode potential of less than about -1.0V; the concentration of Ti being at
3 least 94 atom percent within the target.
- 1 11. The sputtering target of claim 10 wherein the one or more elements are selected
2 from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Mn,
3 V, Y, and Zr.
- 1 12. The sputtering target of claim 10 wherein the one or more elements comprise Zr.
- 1 13. The sputtering target of claim 10 wherein the one or more elements comprise
2 Ta.
- 1 14. The sputtering target of claim 10 wherein the one or more elements comprise Y.
- 1 15. The sputtering target of claim 10 wherein the one or more elements comprise
2 Mg.
- 1 16. The sputtering target of claim 10 wherein the target consists essentially of the Ti
2 and the one or more elements.

- 1 17. The sputtering target of claim 10 wherein the target consists of the Ti and the
2 one or more elements.
- 1 18. The sputtering target of claim 10 wherein the total amount of the one or more
2 elements is in the range of 0.001 atom% to 50 atom%.
- 1 19. The sputtering target of claim 10 wherein the total amount of the one or more
2 elements is in the range of 0.001 atom% to 10 atom%.
- 1 20. A thin film of $Ti_xQ_yN_z$ formed by reactively sputtering the target of claim 10
2 in a nitrogen atmosphere, wherein "Q" is a label for said one or more elements.
- 1 21. The thin film of claim 20 wherein $x=0.3-0.7$, $y=0.001-0.1$, and $z=0.4-0.6$.
- 1 22. The thin film of claim 20 wherein $x=0.3-0.7$, $y=0.001-0.01$, and $z=0.4-0.6$.
- 1 23. The thin film of claim 20 having a thickness of from about 5 nm to about
2 50nm.
- 1 24. The thin film of claim 20 having a thickness of from about 5nm to about
2 20nm.
- 1 25. The thin film of claim 20 further comprising an electrical resistivity of equal
2 to or less than $200\mu\Omega\cdot\text{cm}$.

- 1 26. The $Ti_xQ_yN_z$ thin film of claim 20 used as a Cu barrier layer in a
2 microelectronic device.
- 1 27. The thin film of claim 20 further comprising a grain size of equal to or less
2 than 500nm, the grain size remaining equal to or less than 500nm after the thin
3 film is exposed to a temperature of at least about 500°C for a time of at least
4 about 30 minutes in a vacuum anneal.
- 1 28. The thin film of claim 20 further comprising a grain size of equal to or
2 smaller than 100nm, the grain size remaining equal to or less than 100nm after
3 the thin film is exposed to a temperature of at least about 500°C for a time of at
4 least about 30 minutes in a vacuum anneal.
- 1 29. A thin film of $Ti_xQ_yN_zO_w$ formed by reactively sputtering the sputtering
2 target of claim 10 in the presence of a nitrogen-containing gas and an oxygen-
3 containing gas, wherein "Q" is a label for said one or more elements.
- 1 30. The thin film of claim 29 wherein $x=0.3-0.7$, $y=0.001-0.1$, $z=0.4-0.6$, and
2 $w=0.0001-0.0010$.
- 1 31. The thin film of claim 29 having a thickness of from about 5nm to about
2 50nm.
- 1 32. The thin film of claim 29 having a thickness of from about 5nm to about
2 20nm.

1 33. The thin film of claim 29 further comprising an electrical resistivity of equal
2 to or lower than $200\mu\Omega\cdot\text{cm}$.

1 34. The thin film of claim 29 further comprising a grain size of equal to or less
2 than 500nm, the grain size remaining equal to or less than 500nm after the thin
3 film is exposed to a temperature of at least about 500°C for a time of at least
4 about 30 minutes in a vacuum anneal.

1 35. The thin film of claim 29 further comprising a grain size of equal to or
2 smaller than 100nm, the grain size remaining equal to or less than 100nm after
3 the thin film is exposed to a temperature of at least about 500°C for a time of at
4 least about 30 minutes in a vacuum anneal.

1 36. The $\text{Ti}_x\text{Q}_y\text{N}_z\text{O}_w$ thin film of claim 29 used as a Cu barrier layer in a
2 microelectronic device.

1 37. A sputtering target comprising Ti and one or more elements which have a
2 melting temperature of at least about 2500°C, and which do not react with copper at
3 temperatures at or below the melting temperature.

1 38. The sputtering target of claim 37 wherein the one or more elements are selected
2 from the group consisting of Mo, Ta and W.

1 39. The sputtering target of claim 37 wherein the one or more elements comprise
2 Mo.

1 40. The sputtering target of claim 37 wherein the one or more elements comprise
2 Ta.

1 41. The sputtering target of claim 37 wherein the one or more elements comprise W.

1 42. The sputtering target of claim 37 wherein the target consists essentially of the Ti
2 and the one or more elements.

1 43. The sputtering target of claim 37 wherein the target consists of the Ti and the
2 one or more elements.

1 44. The sputtering target of claim 37 wherein the total amount of the one or more
2 elements is in the range of 0.001 atom% to 50 atom%.

1 45. The sputtering target of claim 37 wherein the total amount of the one or more
2 elements is in the range of 0.001 atom% to 10 atom%.

1 46. A thin film of $Ti_xQ_yN_z$ formed by reactively sputtering the target of claim 37
2 in a nitrogen atmosphere, wherein "Q" is a label for said one or more elements.

1 47. The thin film of claim 46 wherein $x=0.3-0.7$, $y=0.001-0.1$, and $z=0.4-0.6$.

1 48. The $Ti_xQ_yN_z$ thin film of claim 46 used as a Cu barrier layer in a
2 microelectronic device.

1 49. The thin film of claim 46 further comprising a grain size of equal to or less
2 than 500nm, the grain size remaining equal to or less than 500nm after the thin
3 film is exposed to a temperature of at least about 500°C for a time of at least
4 about 30 minutes in a vacuum anneal.

1 50. The thin film of claim 46 further comprising a grain size of equal to or
2 smaller than 100nm, the grain size remaining equal to or less than 100nm after
3 the thin film is exposed to a temperature of at least about 500°C for a time of at
4 least about 30 minutes in a vacuum anneal.

1 51. A thin film of $Ti_xQ_yN_zO_w$ formed by reactively sputtering the sputtering
2 target of claim 37 in the presence of a nitrogen-containing gas and an oxygen-
3 containing gas, wherein "Q" is a label for said one or more elements.

1 52. The thin film of claim 51 wherein $x=0.3-0.7$, $y=0.001-0.1$, $z=0.4-0.6$, and
2 $w=0.0001-0.0010$.

1 53. The thin film of claim 51 having a thickness of from about 5nm to about
2 50nm.

1 54. The thin film of claim 51 having a thickness of from about 5nm to about
2 20nm.

1 55. The thin film of claim 51 further comprising an electrical resistivity of equal
2 to or lower than $200\mu\Omega\cdot\text{cm}$.

1 56. The thin film of claim 51 further comprising a grain size of equal to or less
2 than 500nm, the grain size remaining equal to or less than 500nm after the thin
3 film is exposed to a temperature of at least about 500°C for a time of at least
4 about 30 minutes in a vacuum anneal.

1 57. The thin film of claim 51 further comprising a grain size of equal to or
2 smaller than 100nm, the grain size remaining equal to or less than 100nm after
3 the thin film is exposed to a temperature of at least about 500°C for a time of at
4 least about 30 minutes in a vacuum anneal.

1 58. The $Ti_xQ_yN_zO_w$ thin film of claim 51 used as a Cu barrier layer in a
2 microelectronic device.

1 59. A composition comprising:
2 at least 94 atom% Ti; and
3 one or more elements which have a standard electrode potential of
4 less than about -1.0V.

1 60. The composition of claim 59 consisting of the Ti and the one or more
2 elements.

1 61. The composition of claim 60 wherein the one or more elements are selected
2 from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Y,
3 Mn, V and Zr.

- 1 62. A composition comprising the formula $Ti_xQ_yN_z$, wherein $x=0.3-0.7$, $y=0.001-$
2 0.1, and $z=0.4-0.6$; and wherein "Q" is one or more elements selected from the
3 group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Y, and Zr.
- 1 63. A composition comprising the formula $Ti_xQ_yN_zO_w$, wherein $x=0.3-0.7$,
2 $y=0.001-0.1$, $z=0.4-0.6$, and $w=0.0001-0.0010$; and wherein "Q" is one or more
3 elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg,
4 Nb, Nd, Sc, Sr, Y, and Zr.
- 1 64. A composition comprising the formula $Ti_xQ_yN_z$, wherein $x=0.3-0.7$, $y=0.001-$
2 0.1, and $z=0.4-0.6$; and wherein "Q" is one or more elements selected from the
3 group consisting of Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Si, P, S,
4 Sc, Cr, Mn, Fe, Co, Ni, Y, and In.
- 1 65. A composition comprising the formula $Ti_xQ_yN_zO_w$, wherein $x=0.3-0.7$,
2 $y=0.001-0.1$, $z=0.4-0.6$, and $w=0.0001-0.0010$; and wherein "Q" is one or more
3 elements selected from the group consisting of Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd,
4 Dy, Ho, Er, Yb, Si, P, S, Sc, Cr, Mn, Fe, Co, Ni, Y, and In.
- 1 66. A method of inhibiting copper diffusion into a substrate, comprising:
2 forming a first layer comprising Ti and one or more elements over the
3 substrate, the one or more elements having a difference in atomic radii
4 relative to Ti of at least 10%; and
5 forming a copper-containing layer over the first layer and separated
6 from the substrate by the first layer; the first layer inhibiting copper diffusion
7 from the copper-containing layer to the substrate.

- 1 67. The sputtering target of claim 66 wherein the one or more elements are selected
2 from the group consisting of Si, P, S, Sc, Cr, Mn, Fe, Co, Ni, Y and In.
- 1 68. The sputtering target of claim 66 wherein the one or more elements have a
2 difference in atomic radii of at least 20% relative to Ti.
- 1 69. The sputtering target of claim 68 wherein the one or more elements are selected
2 from the group consisting of Be, B, C, Mo, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and
3 Yb.
- 1 70. The sputtering target of claim 68 wherein the one or more elements comprise C.
- 1 71. The sputtering target of claim 68 wherein the one or more elements comprise B.
- 1 72. A method of inhibiting copper diffusion into a substrate, comprising:
2 forming a first layer comprising Ti and one or more elements which
3 have a standard electrode potential of less than about -1.0V over the
4 substrate; and
5 forming a copper-containing layer over the first layer and separated
6 from the substrate by the first layer; the first layer inhibiting copper diffusion
7 from the copper-containing layer to the substrate.
- 1 73. The method of claim 72 wherein the one or more elements are selected from the
2 group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nb, Nd, Sc, Sr, Mn, V, Y, and
3 Zr.

1 74. The method of claim 73 wherein the target consists essentially of the Ti and the
2 one or more elements.

1 75. The method of claim 73 wherein the target consists of the Ti and the one or
2 more elements.

1 76. The method of claim 73 wherein the target is sputtered in an atmosphere
2 comprising nitrogen-containing components to form the first layer to comprise
3 nitrogen in addition to the titanium and the one or more elements.

1 77. The method of claim 73 wherein the target is sputtered in an atmosphere
2 comprising nitrogen-containing components and oxygen-containing components to
3 form the first layer to comprise nitrogen and oxygen in addition to the titanium and the
4 one or more elements.

1 78. The method of claim 72 wherein the one or more elements comprise Zr.

1 79. The method of claim 72 wherein the one or more elements comprise Ta.

1 80. The method of claim 72 wherein the one or more elements comprise Y.

1 81. The method of claim 72 wherein the one or more elements comprise Mg.

- 1 82. The method of claim 72 wherein the first layer is formed by sputter deposition
2 from a target comprising the Ti and the one or more elements which have a standard
3 electrode potential of less than about -1.0V.

ABSTRACT OF THE DISCLOSURE

The invention described herein relates to new titanium-comprising materials which can be utilized for forming titanium alloy sputtering targets. The titanium alloy sputtering targets can be reactively sputtered in a nitrogen atmosphere to form an alloy TiN film, or alternatively in a nitrogen and oxygen atmosphere to form an alloy TiON thin film. The thin films formed in accordance with the present invention can have a non-columnar grain structure, low electrical resistivity, high chemical stability, and barrier layer properties comparable to those of TaN. Further, the titanium alloy sputtering target materials produced in accordance with the present invention can be more cost-effective for semiconductor applications than are high-purity tantalum materials. In one aspect, the invention encompasses a sputtering target comprising Ti and one or more elements which have a standard electrode potential of less than -1.0 volt. In another aspect, the invention encompasses a method of inhibiting copper diffusion into a substrate. A first layer comprising titanium and one or more elements which have a standard electrode potential of less than -1.0V is formed over the substrate. A copper-containing layer is then formed over the first layer and separated from the substrate by the first layer. The first layer inhibits copper diffusion from the copper-containing layer to the substrate. The invention also encompasses a sputtering target comprising Ti and one or more elements which have melting temperatures greater than or equal to 2500°C.

The one or more elements do not react with copper at temperatures of less than or equal to the melting temperatures of the one or more elements.

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APPLICATION FOR LETTERS PATENT

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High Purity Tantalum, Methods of Increasing Tantalum
Purity, and Electrolysis Apparatuses for Producing
Tantalum

* * * * *

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High Purity Tantalum, Methods of Increasing Tantalum Purity, and Electrolysis Apparatuses for Producing Tantalum

TECHNICAL FIELD

5 The invention pertains to methods of increasing tantalum purity, and to electrolysis apparatuses for producing tantalum. The invention also pertains to high purity tantalum.

BACKGROUND OF THE INVENTION

10 High purity tantalum can have numerous applications. For instance, tantalum can be utilized in the semiconductor industry for forming conductive components such as, for example, conductive capacitor components. Tantalum can also be utilized for formation of diffusion barriers between copper films and silicon substrates. For instance, tantalum can be sputter-deposited over a silicon substrate in an argon/nitrogen ambient to form a
15 thin TaN layer which can function as a diffusion barrier layer between a copper-containing material and a silicon substrate to alleviate or prevent copper diffusion from the copper material to the silicon substrate. In other applications, high purity tantalum can be incorporated into targets comprising tantalum and silicon, and such targets can be sputtered in an argon/nitrogen ambient to produce tantalum-silicon-nitrogen thin films,
20 which can, in particular applications, be even more desirable than TaN films for application as diffusion barrier layers. It is noted that tantalum-silicon-nitrogen thin films can also be formed by sputtering a high purity tantalum target in an ambient comprising argon, silane and nitrogen.

 The numerous potential uses for tantalum has created a demand for high purity
25 tantalum sputtering targets. It can be problematic to produce high purity tantalum in sufficient quantities to meet current demand for the material. It would, therefore, be desirable to develop new methods for purification of tantalum. Tantalum halide compounds are relatively common forms of impure tantalum, with an exemplary compound being K_2TaF_7 . It would, accordingly, be desirable to develop new methods

which could utilize tantalum halide compounds as starting materials for forming purified tantalum.

SUMMARY OF THE INVENTION

5 In one aspect, the invention encompasses a method of producing high purity tantalum through a chemical reduction reaction. A first tantalum-containing composition is provided, and has tantalum therein at a first purity level. The first tantalum-containing composition is placed within an electrolysis apparatus. The electrolysis apparatus comprises a liquid-retaining vessel, a cathode, an anode, and a collector between a lower
10 portion of the cathode and the vessel. The first tantalum-containing composition is exposed to a current within the electrolysis apparatus to electrolytically separate the tantalum from other components of the first tantalum-containing composition. The separated tantalum is collected in the collector. The collected tantalum is removed from the electrolysis apparatus as a product material. The product material has tantalum
15 therein at a second purity level which is higher than the first purity level.

 In another aspect, the invention encompasses a method of increasing tantalum purity. A starting composition which includes a compound comprising tantalum and a halogen is provided. The composition is provided within an electrolysis apparatus as a solution. The electrolysis apparatus includes a vessel having a cathode extending
20 therein. A collector is between the vessel and a lower portion of the cathode. The composition is exposed to a current within the electrolysis apparatus to electrolytically separate the tantalum of the compound from the halogen. The separated tantalum is collected in the collector, and subsequently removed from the electrolysis apparatus as a product material. The product material has a higher tantalum purity than the starting
25 composition.

 In another aspect, the invention encompasses an electrolysis apparatus for producing tantalum. The apparatus includes a liquid-retaining vessel, and a tantalum-comprising liquid within the vessel. The apparatus further includes a cathode extending

into the liquid, and a basket surrounding a lower portion of the cathode. Additionally, the apparatus comprises an anode contacting the liquid, and a power source providing electrical current between the anode and cathode.

In yet another aspect, the invention encompasses a high purity tantalum composition.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic, cross-sectional view of a first embodiment apparatus encompassed by the present invention.

Fig. 2 is a diagrammatic, cross-sectional view of a second embodiment apparatus encompassed by the present invention.

Fig. 3 is a diagrammatic, cross-sectional view of a third embodiment apparatus encompassed by the present invention.

Fig. 4 is a diagrammatic, cross-sectional view of a fourth embodiment apparatus encompassed by the present invention.

Fig. 5 is a diagrammatic, cross-sectional view of an exemplary physical vapor deposition target encompassed by the present invention.

Fig. 6 is a top view of the target of Fig. 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention encompasses improved methodology for electrolytic purification of tantalum. For purposes of interpreting this disclosure and the claims that follow, a process is defined to "purify" tantalum if it produces a tantalum-containing product having a higher concentration of tantalum than a tantalum-containing starting material provided to the process. Thus, a process that converts K_2TaF_7 to relatively pure Ta is considered herein to be a tantalum purification process, even though it is recognized that

the tantalum produced by the process has a different chemical form than the tantalum of the K_2TaF_7 feed material.

A previous process that has been utilized for purification of tantalum is a reduction method in which sodium metal is combined with a source of Ta. The sodium metal is highly reactive, and violent reactions can occur. Further, separation of products resulting from the reduction method can be labor intensive and expensive. Accordingly, electrolytic purification can be less hazardous than prior art reduction methods for Ta production.

Methodology of the present invention can be utilized for various electrolytic purification processes, including electrowinning and electrorefining. In a particular aspect, the invention pertains to electrowinning of tantalum. The tantalum can be provided in the form of a raw material (also referred to herein as a starting material) having tantalum in a relatively impure form. The raw material can comprise a tantalum composition, such as, for example, a compound comprising tantalum and a halogen (such as, for example, K_2TaF_7 or $TaCl_5$), or a compound comprising tantalum and oxygen (such as, for example, Ta_2O_5). The raw material can be initially partially purified by non-electrolytic methods. For instance $TaCl_5$ can be partially purified by fractional distillation, and K_2TaF_7 can be partially purified by recrystallization.

In accordance with methodology of the present invention, the raw material is eventually subjected to electrolytic purification. The raw material can be placed in an electrolysis apparatus within a molten salt media to function as an electrolyte. The molten salt media can comprise, for example, one or both of NaCl and KCl, and in a particular embodiment comprises a eutectic mixture of NaCl and KCl. Preferably, the mixture will be non-aqueous, as any water which is present could lead to evolution of hydrogen at a cathode of electrolytic apparatus, and cause complications with tantalum collection.

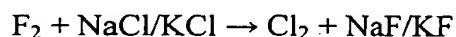
An exemplary electrolyte can comprise from about 5% to about 50% K_2TaF_7 (by weight), and the remainder being a eutectic mixture of KCl and NaCl. Preferred

electrolyte compositions can comprise from about 20% to about 35% K_2TaF_7 (by weight), and the remainder being a eutectic mixture of KCl and NaCl. It is found that if the concentration of K_2TaF_7 is maintained within the preferred range, a current efficiency of tantalum purification can be maintained at about 80%. It is also found that

5 temperature can effect the current efficiency, and it can be preferred to maintain the electrolyte at a temperature of from about 730°C to about 770°C during purification of tantalum.

During electrolysis, positive Ta^{5+} ions are reduced to metal at a cathode of the electrolytic apparatus, and negative F^- ions form fluorine gas at the anode. Preferably,

10 chloride salts are provided within the electrolyte solution to allow exchange of electrons from $2Cl^-$ to F_2 and thereby form Cl_2 and $2F^-$. For instance, a molten solution comprising NaCl/KCl can undergo the following reaction:



Such reaction takes place because fluorine is a stronger oxidant than chlorine.

15 The conversion of diatomic fluorine gas to diatomic chlorine gas can be desirable for environmental and personal safety reasons, in that chlorine is less corrosive than fluorine. Numerous chloride salts can be included in a molten electrolyte solution to enable conversion of diatomic fluorine gas to diatomic chlorine gas, including, for example, lithium chloride, cesium chloride, and, of course, the above described sodium

20 chloride and potassium chloride. It can be preferred to replenish NaCl and/or KCl in an electrolysis apparatus of the present invention to keep the total concentration of KF and NaF to below about 15%.

In particular embodiments of the present invention, an anode of the electrolytic apparatus comprises graphite. In such embodiments, it can be desirable to include oxides

25 within a molten salt bath, in that the oxides can generate diatomic oxygen which will subsequently react with the anode to produce carbon monoxide and/or carbon dioxide from a surface of the anode and thus produce a fresh surface of the anode for further reaction during an electrolysis process. The production of a fresh anode surface can

improve efficiency of the electrolysis process. If an oxide is to be added to the molten material, it can be preferred that the oxide be tantalum oxide (Ta_2O_5), and in particular it can be preferred that any oxides present in the molten material consist essentially of, or consist of, tantalum oxide. Such preference is due to the ultimate goal of purifying
5 tantalum materials within the electrolytic apparatuses of the present invention, and accordingly it is desired to avoid providing metallic components other than tantalum within the apparatus to avoid providing sources of contaminants.

It is noted that the above-described process for providing oxides within a molten electrolyte solution of the present invention can occur in particular embodiments of
10 methodology of the present invention, but that it can be preferred to avoid providing oxides in some embodiments of the present invention. For instance, some embodiments of the present invention utilize a graphite liner to retain an electrolyte solution during electrolysis process. In such embodiments it can be preferred to avoid providing oxides within the electrolytic solution in that the oxides can cause consumption of the graphite
15 liner, and possibly cause eventual failure of the liner.

Particular embodiments of the present invention are described with reference to Figs. 1-4. Referring initially to Fig. 1, an apparatus 10 is shown diagrammatically in cross-sectional side view. Apparatus 10 comprises a liquid retaining vessel 12. Vessel 12 includes a graphite inner liner 14 within a structural support 16. Structural support 16
20 can comprise, for example, iron. Liner 14 and support 16 can be referred to as inner and outer materials, respectively, of vessel 12. Liner 14 has an inner sidewall 18 which defines an interior periphery of vessel 12.

A liquid 20 is retained within vessel 12, and can comprise, for example, a molten mixture of sodium chloride and potassium chloride, together with a source of tantalum.
25 The tantalum source can comprise, for example, a compound having tantalum and a halogen (such as, for example, K_2TaF_7 or $TaCl_5$), and/or other forms of tantalum, such as compounds having tantalum and oxygen (such as, for example, Ta_2O_5). Liquid 20 is an electrolyte of the electrolysis apparatus 10, and can be referred to as a tantalum-

comprising electrolyte. Liquid 20 contacts only liner 14, and does not contact outer structural support 16.

A lid 22 is shown provided over liquid 20, and supported by liner 14. Lid 22 can comprise, for example, graphite. Lid 22 has an opening 24 extending therein. A cathode 26 is provided through opening 24 and extends into liquid 20. Cathode 26 is connected to an electrical power source 28. Power source 28 is also connected to graphite liner 14, and accordingly graphite liner 14 can function as an anode in electrolytic apparatus 10.

In operation, power source 28 is utilized to provide an electrical current between cathode 26 and graphite liner 14, and accordingly defines an electrical circuit comprising graphite liner 14, liquid 20 and cathode 26. Cathode 26 can comprise, for example, a nickel rod 30 extending downwardly through opening 24 and connected with a tantalum lower section 32. Cathode 26 can be operated at a cathode current density of, for example, from about 0.7 A/cm^2 to about 1.3 A/cm^2 .

A basket 34 is shown provided within liquid 20, and extending around a lower portion of cathode 26. Basket 34 will comprise a mesh (not shown) allowing liquid 20 to flow through basket 34. Basket 34 is shown supported over graphite liner 14 by a support structure 36. Support structure 36 can comprise, for example, an electrically insulative material, such as, for example, a ceramic material. Basket 34 is preferably electrically isolated from anode 14. Basket 34 can also be electrically isolated from cathode 26, or, in particular embodiments, can be electrically connected with cathode 26 (for example, the embodiment of Fig. 2 has a basket electrically connected with a cathode). In embodiments in which basket 34 is electrically connected with cathode 26, the basket can comprise an electrically conductive material. Regardless of whether basket 34 is electrically connected with cathode 26, it is preferred that basket 34 comprise a material which will minimize or alleviate contamination of tantalum materials ultimately formed on cathode 26. Accordingly, it can be preferred that basket 34 comprise tantalum. Alternatively, basket 34 can comprise, consist of, or consist

essentially of, one or more of tantalum, nickel, cobalt and molybdenum; with an exemplary material being a nickel/chromium alloy, such as Inconel.

Basket 34 is an exemplary example of a tantalum collector that can be provided between a lower portion of cathode 26 and vessel 16. Other current collector
5 embodiments include, for example, flat plates extending beneath a bottom portion of cathode 26. The shown basket 34 surrounds a lower portion of cathode 26. Such can be advantageous for maximally retaining tantalum particles sloughing from a surface of cathode 26. However, it is to be understood that the invention encompasses other
10 embodiments of tantalum collectors which do not extend around cathode 26, but which are instead below cathode 26 in their entirety.

In operation, the electrical current provided between cathode 26 and anode 14 causes tantalum from liquid 20 to be deposited on cathode 26 as a layer 40. Such layer is powdery as formed, and accordingly tantalum sloughs from layer 40 and collects within
15 basket 34 as a mass 42. Mass 42 can comprise, for example, a powdery texture. Basket 34 preferably has a pore size which retains the majority of the sloughed powder. In particular embodiments, basket 34 can have meshed sidewalls, but a solid floor; with the solid floor being provided to alleviate loss of powder that can occur through a meshed floor.

The tantalum of mass 42 is purer than the tantalum initially provided within
20 liquid 20 as a starting composition. Among the contaminants that can be removed by the electrolytic process of Fig. 1 are halogens, and various metallic contaminants.

The electrolysis of Fig. 1 also, of course, comprises a reaction at anode 14. If a starting material is, for example, K_2TaF_7 , then diatomic fluorine (F_2) can form at anode 14 as a gas. Such gas can subsequently interact with chlorine ions within liquid 20 to
25 form products of diatomic chlorine gas (Cl_2) and fluorine ions (F^-). If all of the diatomic fluorine reacts, than chlorine gas can be the only product gas exiting from liquid 20. However, it is typical that all of the diatomic fluorine does not react, and accordingly both diatomic fluorine and diatomic chlorine gases exit from liquid 20. The gases

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exiting liquid 20 proceed upwardly through opening 24. A purpose of lid 22 can be to protect outer portion 16 of vessel 12 from interaction with the corrosive diatomic chlorine and/or diatomic fluorine gases. For instance, if portion 16 comprises iron, then diatomic chlorine and fluorine gases can corrode the iron. However, lid 22 can direct the gases through opening 24, and subsequent piping or tubing (not shown in Fig. 1) can be utilized to direct the gases to a chamber where the gases can be condensed or otherwise reclaimed. An advantage of having an upper portion of cathode 26 made of nickel is that such upper portion will be exposed to the diatomic halogen gases, and nickel can be relatively resistant to corrosion compared to other materials, such as, for example, tantalum. Also, nickel can be cheaper to utilize than tantalum. An advantage of having lower portion 42 of cathode 26 as tantalum is that such can alleviate contamination of the deposited tantalum material 40 relative to that which would occur if lower portion 32 were made of a material other than tantalum.

After formation of a desired quantity of mass 42 within basket 34, the mass 42 can be removed from within basket 34. Such removal can comprise, for example, lifting basket 34 from within liquid 20 and dumping the mass out of the basket. Alternatively, such removal can comprise, for example, inserting a device within basket 34 to lift mass 42 from within basket 34. An exemplary device which can be inserted into basket 34 to lift mass 42 is a vacuum device. It is noted that if basket 34 is lifted from liquid 20 prior to removal of mass 42 from within the basket, the basket can be provided with a openable bottom portion that is opened to remove mass 42. An openable bottom portion can be achieved as, for example, a bottom portion attached to the rest of basket 34 as a hinged door that can be opened to release mass 42 from within the basket.

In the shown embodiment, basket 34 extends only partially within liquid 20. However, it is to be understood that the invention encompasses other embodiments wherein basket 34 is entirely submerged within liquid 20.

Cathode 26 can be mounted to a support structure (not shown) coupled to a power source so that cathode 26 can be lifted through opening 24 and removed from

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within liquid 20. Such lifting of cathode 26 from within liquid 20 can simplify removal of tantalum-comprising layers 40 from the cathode, and can simplify replacement of cathode 26 if excessive corrosion of the cathode occurs.

Although apparatus 10 is shown and described as a batch-type apparatus, it is to be understood that the apparatus can also be configured for continuous production of tantalum. For instance, tantalum-comprising compositions can be continuously flowed into electrolyte 20, and tantalum-comprising mass 42 can be continuously extracted from within basket 34. Alternatively, tantalum-comprising starting compositions can be semi-continuously flowed into electrolyte 20 during collection of mass 42 within basket 34 and/or during extraction of mass 42 from within basket 34.

Referring next to Fig. 2, a second embodiment apparatus 100 is illustrated. Apparatus 100 comprises a liquid-retaining vessel 102 which includes an inner vessel liner 104 and an outer vessel component 106. Inner vessel liner 104 and outer vessel component 106 can have identical constructions to those discussed above with reference to liner 14 and outer vessel component 16 in Fig. 1. Specifically, liner 104 can comprise graphite, and outer component 106 can comprise iron. However, a difference between apparatus 100 of Fig. 2 and apparatus 10 of Fig. 1 is that liner 104 is not an anode of apparatus 100. Accordingly, liner 104 can comprise a non-conductive material, such as, for example, a ceramic material. It can, however, be preferred to utilize graphite instead of a ceramic material for liner 104 in that it is found that metallic components from support 106 can migrate through a ceramic material to contaminate a tantalum mass produced in apparatus 100. In particular embodiments, such contamination can be minor, and can be avoided by utilization of appropriate compositions for outer component 106. Accordingly, it is possible, although generally not preferred, to utilize a ceramic material for liner 104.

A liquid 110 is provided within vessel 102. Liquid 110 can comprise, for example, identical constituents to those discussed above regarding liquid 20 of Fig. 1, and can therefore comprise potassium chloride, sodium chloride, and K_2TaF_7 .

FIG. 10/10

A cathode 112, and an anode 114 are provided within liquid 110. Cathode 112 can comprise, for example, an identical construction to that described above for cathode 26 of Fig. 2, and can accordingly comprise a nickel-containing upper portion 116 over a tantalum-comprising lower portion 118. Anode 114 can comprise, for example, graphite.

5 Cathode 112 and anode 114 are electrically connected through a power source 120. Power source 120 provides a current between cathode 112 and anode 114, and accordingly defines a circuit comprising cathode 112, anode 114 and liquid 110.

A tantalum collector 122 is provided between a lower portion of cathode 116 and vessel 102; and in the shown embodiment is in the form of a basket 122 provided around
10 a lower portion of cathode 116. Basket 122 is shown electrically connected to cathode 116 through an electrically conductive interconnect 124. Basket 122 can comprise, consist of, or consist essentially of, various electrically conductive materials, such as, for example, tantalum, molybdenum, nickel and/or cobalt. In a particular embodiment, basket 122 consists essentially of, or consists of, tantalum.

15 A difference between the embodiment of Fig. 2 and that of Fig. 1 is that basket 122 can be positioned directly on liner 104 in the embodiment of Fig. 2, whereas basket 34 was isolated from liner 14 in the embodiment of Fig. 1. A reason that cathode 122 can be positioned on liner 104 is that liner 104 is not the anode of the embodiment of Fig. 2. The shown placement of basket 122 on liner 104 presumes that liner 104 is an
20 electrically insulative material, such as, for example, a ceramic. If liner 104 is instead a conductive material, such as, for example, graphite, it can be preferred to electrically isolate basket 12 from liner 104 utilizing, for example, an electrically insulative spacer similar to the spacer 36 described above with reference to Fig. 1. If basket 122 were provided directly on a conductive liner 104, then an entirety of the conductive liner 104
25 could become a cathode of electrolytic apparatus 100, which could result in tantalum being deposited around a periphery of liner 104, as well as within basket 122, which could complicate collection of tantalum.

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In operation, electrolytic apparatus 100 is utilized to form tantalum layers 140 on cathode 112. Subsequently, tantalum can slough from layers 140 to form a mass 142 within basket 122. Mass 142 collects within basket 122, and can subsequently be removed from basket 122 as relatively pure tantalum. The removal of mass 142 can be accomplished by one or more of the methods described above for removal of mass 42 from the basket 34 of Fig. 1. Such methods can include lifting basket 122 from liquid 110. If basket 122 is to be lifted, it can be preferred to have electrical interconnect 124 be either long and flexible (such as, for example, a long wire) or removable from basket 122 so that basket 122 can be lifted separately from cathode 112. Alternatively, it can be desirable to have electrical interconnect 124 be short and stiff so that basket 122 can be lifted by lifting of cathode 112.

It is noted that a difference between the embodiment of Fig. 2 and that of Fig. 1 is that Fig. 1 illustrates a lid (22) formed over an electrolytic solution, and the embodiment of Fig. 2 does not comprise such lid. However, it is to be understood that a similar lid could be provided in the embodiment of Fig. 2. Also, it is to be understood that although only one anode 114 and cathode 112 are shown provided within liquid 110, a plurality of anodes and/or a plurality of cathodes could be utilized. A difficulty in utilizing a plurality of cathodes can be in providing all the cathodes over a tantalum collector (or within a basket), or in providing separate tantalum collectors (such as baskets) for various individual cathodes. Accordingly, it can be preferred to utilize only one cathode. However, similar problems do not exist with anode 114, and accordingly it can be preferred to utilize numerous anodes in order to increase the current efficiency of apparatus 100.

The shown liner 104 can be optional, and the invention encompasses apparatuses similar to 100, but wherein outer structural component 106 is the only component of vessel 102. In such embodiments, component 106 can comprise graphite, or it can comprise a metal, such as, for example, iron. A difficulty in utilizing iron as the only component of vessel 102 is that liquid 110 will then be in contact with the iron, and

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accordingly, iron can be leached from vessel 106 and into liquid 110 to provide contaminating metallic components within tantalum mass 142. Further, if one or both of the corrosive gases Cl_2 and F_2 contact iron, the iron can corrode to release contaminating iron materials into liquid 110. Accordingly, it can be less desirable to utilize a vessel

5 102 having an iron component 106 as the only vessel component, rather than having the iron component 106 lined with a different component, such as, for example, a graphite or ceramic liner 104.

Fig. 3 illustrates a third embodiment apparatus 300. Apparatus 300 comprises a liquid-retaining vessel 302 which includes a graphite liner 304 and a stainless steel retort

10 306. The liner 304 and retort 306 are within a furnace 307. A liquid 310 is provided within vessel 302. Liquid 310 can comprise, for example, identical constituents to those discussed above regarding liquid 20 of Fig. 1, and can therefore comprise potassium chloride, sodium chloride, and K_2TaF_7 .

Graphite liner 304 connects with a graphite lid 322, which in turn connects with a

15 vertical graphite extension 309. Extension 309 defines a portion of a vertically-extending graphite tube 308 extending upwardly above liquid 310. Graphite extension 309 connects with an additional vertical graphite extension 311 that defines another portion of the graphite tube 308. A valve 315 is provided across graphite tube 308 to enable control of gas flow through the tube. The tube 308 terminates in a tee 317. Gases

20 flowing upwardly through tube 308 are directed through tee 317 to collection and/or disposal apparatuses which are not shown in Fig. 3.

A stainless steel retort lid 323 extends horizontally relative to graphite extension 309, and is over graphite lid 322.

A cathode 312 is provided within liquid 310. Cathode 312 can comprise, for

25 example, an identical construction to that described above for cathode 26 of Fig. 2, and can accordingly comprise a nickel-containing upper portion 316 over a tantalum-comprising lower portion 318. In a particular embodiment, upper portion 316 consists

essentially of nickel, and lower portion 318 consists essentially of, or consists of, tantalum.

Graphite liner 304 can be an anode of the electrolysis apparatus 300, and can accordingly be connected to cathode 312 through a power source (not shown).

5 A basket 334 is suspended in liquid 310 by a support structure 333. Support structure 333 can be utilized for lifting of basket 334 from liquid 310, as well as for lowering basket 334 into liquid 310. Basket 334 can comprise, consist of, or consist essentially of, various electrically conductive materials, such as, for example, tantalum, molybdenum, nickel and/or cobalt. In a particular embodiment, basket 334 consists
10 essentially of, or consists of, tantalum.

In operation, electrolytic apparatus 300 is utilized to form a tantalum layer 340 on cathode 312. Subsequently, tantalum can slough from layer 340 to form a mass 342 within basket 334. Mass 342 collects within basket 334, and can subsequently be removed from basket 334 as relatively pure tantalum. The removal of mass 342 can be
15 accomplished by one or more of the methods described above for removal of mass 42 from the basket 34 of Fig. 1.

Fig. 4 illustrates a fourth embodiment apparatus 400. Apparatus 400 is similar to apparatus 300, and identical numbering is utilized in labeling the structures of Fig. 4 as was utilized in labeling the structures of Fig. 3. A difference between the apparatus 400
20 of Fig. 4 and the apparatus 300 of Fig. 3 is that apparatus 400 comprises a feed hopper 402 to enable feeding of a tantalum-containing starting material directly into basket 334 during electrolytic purification of the tantalum from the starting material. The feeding of tantalum-containing starting material into basket 334 can enable control of a concentration of Ta^{5+} ions proximate cathode 312. If tantalum-containing starting
25 material is not introduced proximate cathode 312, the concentration of Ta^{5+} ions proximate the cathode can decrease monotonically after each run of tantalum-containing material through an electrolytic purification apparatus. The tantalum-containing starting material preferably melts upon being introduced proximate cathode 312, and thus does

not contaminate solid tantalum product 342 (e.g., tantalum powder) that is being collected within basket 334. The tantalum-containing starting material can be continuously fed through hopper 402 and into basket 334 during collection of tantalum product 342 within the basket, or can be intermittently fed into basket 334 during the collection.

5

Current Efficiency Determinations

Current efficiency, as function of current density, was determined for various embodiments of the present invention. In an exemplary determination of current efficiency for the embodiment of Fig. 3, several runs were conducted at 750°C in a salt bath containing 25% K_2TaF_7 , with the remainder of the salt bath being a eutectic mixture of NaCl and KCl. The current efficiency of each run was calculated according to Faraday's Law:

$$THW = (C \times \text{at. wt.}) / (\text{Val.} \times 96485) \quad \text{---} \quad (\text{Equation 1})$$

$$\%CE = (AHW/THW) \times 100 \quad (\text{Equation 2})$$

Where:

THW = Theoretical Harvest Weight

AHW = Actual Harvest Weight

C = coulombs = amps x run time in seconds

at. wt. = atomic weight

Val. = valence

%CE = Percent current efficiency.

The current efficiency was determined after a five-step solvent removal of entrained salts that is described below.

Example 1

An apparatus of the type described with Fig. 3 was utilized for purifying tantalum from a molten salt containing 25% K_2TaF_7 in sodium chloride and potassium chloride, at a temperature of $750^\circ C$. It was found that with increasing current density, current efficiency first increases and then decreases. A current efficiency of more than 80% can be achieved when current density is in the range of 0.7 to $1.5 A/cm^2$. It was also found that the process can be operated semi-continuously over an extended period of time by replenishment of the K_2TaF_7 , $NaCl$ and KCl .

Further purification of Tantalum product

A. Solvent removal of entrained salts

5 The tantalum materials produced from methodology of the present invention can have relatively high purity if a graphite liner is utilized in the apparatus described with reference to Fig. 3, and if tantalum is utilized as a cathode and as basket material. For instance, tantalum mass 42 can have a purity of about 99%. The purity can be further improved by rinsing entrained salt from the product and subsequent sintering and/or e-beam melting. Exemplary purification processes are as follows.

10 The removal of entrained salt can be accomplished by, for example, leaching the tantalum product removed from either basket 34 (Fig 1), basket 122 (Fig. 2) or basket 334 (Figs. 3 and 4) with acid or other solvents to remove the salt; or by pulverizing the tantalum product and subsequently flushing the salt from the product with water (preferably high-purity water, such as deionized water).

15 The pulverizing and flushing with water can be a preferred method, and can comprise the following steps:

Step 1, Soak harvested tantalum product (tantalum powder/salt mix) in deionized water overnight;

20 Step 2, Decant the water and pulverize the tantalum powder/salt mix for about 10 minutes in deionized water to form a pulverized mixture;

Step 3, Rinse the pulverized mixture 4-5 times with deionized water, test the turbidity of each rinse;

Step 4, Repeat Steps 1 through 3, four to five times until the turbidity is <20 Nephelometric Turbidity Units (NTU); and

25 Step 5, Dry the resultant powder for at least about four hours at a temperature of at least about 110°C in a vacuum drying oven.

Tantalum powders harvested from an electrolysis apparatus of the present invention and subsequently treated by the pulverization and water rinse of Steps 1-5 can be about 99% pure in tantalum, as determined by Glow Discharge Mass Spectrometry (GDMS) analysis. Analyses of three representative runs after treatment by Steps 1-5 are shown in Table 1 below, with the elemental impurity concentrations listed in parts per million (ppm).

TABLE 1. Representative results of GDMS analysis

element	Sample 1	Sample 2	Sample 3
Na	43	15	10
K	450	150	120
Fe	3000	5000	2000
Ni	3000	5000	2500
Nb	65	90	30

B. E-beam melting.

The Ta powder cleaned per the procedure described in Steps 1-5 can be further purified with sintering and one or more e-beam melting processes. In an exemplary process, the powder is first pressed into cylindrical compacts under a pressure of about 40 ksi. The compact densities can range from about 63% to about 68% of theoretical density. The compacts are then sintered in a vacuum annealing furnace at about 1200°C for about 2 hours. The sintered compacts are sorted by purity into two lots for e-beam melting. The e-beam melting can be performed using a gun-power of about 15 kW-20 kW at a voltage of about 35-45 kV. The pattern used can be a double concentric circular raster, cycled at from about 3 hertz to about 10 hertz. The chamber pressure during the melt can be below 10^{-4} torr. The lower purity lot was melted once to condition the e-beam furnace. The other lot was double melted with samples taken after each melt. Both samples, denoted as 1st melt and 2nd melt, were then analyzed by GDMS. Table 2

shows the results of the GDMS analysis. Elements not listed in Table 2 were below detectable limits. Gas content of the melted samples is listed in Table 3.

Table 2
GDMS results (ppm) and the metallic purity (%) of the e-beam melted samples

Element	1 st Melt	2 nd Melt
Na	1.4	0.37
K	-	0.01
Mg	0.006	-
Si	0.19	0.09
Ti	0.006	0.005
V	0.07	0.02
Cr	1.2	1.3
Fe	25	6.9
Co	0.05	0.01
Ni	4.9	1.8
Cu	0.21	0.26
Zr	0.02	0.02
Nb	27	22
Mo	4.7	2.6
W	1.4	1.6
Re	0.05	0.05
Total	66.20	37.04
purity	99.9934%	99.9963%

5

Table 3
Gas content of the e-beam melted samples

Element	1 st Melt	2 nd Melt
O	20	12
N	3	1.5
S	0.04	0.01

10

Tables 2 and 3 evidence that e-beam melting can be a powerful refining process for tantalum. At a temperature of at least 2994°C (the melting point of Ta), most impurity elements are vaporized in the e-beam melting process. During sintering at 1200°C, some low melting elements such as K, Na and Mg may be also removed. But elements like Fe, Ni, Mo, Nb, W can generally not be effectively removed by vacuum sintering. Repeated e-beam melting has proven to be effective to further improve the purity of tantalum. In Table 2, it can be seen that most elements were further reduced by the second e-beam melt. It is noted that even Nb content was lowered by e-beam melting

(with Nb being understood to typically be difficult to remove from Ta). The Nb content was reduced to below 30ppm by the e-beam melting.

Table 3 evidences that tantalum produced in accordance with the present invention can have very low oxygen and nitrogen contents. Specifically, oxygen is about 20ppm after the first e-beam melt and it is further reduced to 12ppm by the second e-beam melt; nitrogen is 3ppm for first melt and 1.5ppm for the second melt. Accordingly, methodology of the present invention can produce tantalum having less than 70 ppm oxygen, and in particular applications less than 30 ppm oxygen, less than 15 ppm oxygen, or less than 13 ppm oxygen. In yet other particular applications, methodology of the present invention can produce tantalum having less than or equal to about 12 ppm oxygen. Methodology of the present invention can also produce tantalum having less than 25 ppm nitrogen, and in particular applications less than 10 ppm nitrogen, less than 5 ppm nitrogen, or less than 3 ppm nitrogen. In yet other particular applications, methodology of the present invention can produce tantalum having less than or equal to about 1.5 ppm nitrogen. The tantalum of particular applications can be at least 99% pure, is preferably at least 99.95% pure, and is more preferably at least 99.995% pure, by weight.

Tantalum produced in accordance with methodology of the present invention can be formed into physical vapor deposition targets (such as, for example, sputtering targets), and subsequently utilized for sputter-deposition of tantalum-comprising films. It can be advantageous to reduce the concentration of nitrogen and/or oxygen in tantalum-comprising physical vapor deposition targets because such can result in better-quality sputter-deposited films being produced from the targets. For instance, reduction of nitrogen and/or oxygen in a tantalum-comprising sputtering target can reduce particle generation during film deposition, and can result in improved conductivity of a deposited film.

An exemplary physical vapor deposition target 200 is shown in Figs. 5 and 6. Target 200 comprises a surface 202 from which material is to be sputtered during a

sputter-deposition process. Target 200 is an exemplary target which can encompass tantalum materials produced in accordance with methodology of the present invention. Target 200 is representative of a particular type of targets known as Endura™ targets. It is to be understood that tantalum materials of the present invention can be formed into
5 other target shapes besides the shown Endura™ target shape.

CLAIMS

1. A method of producing high purity tantalum, comprising:
 - providing a first tantalum-containing composition, the first tantalum-containing composition having tantalum therein at a first purity level;
 - 5 placing the first tantalum-containing composition within an electrolysis apparatus; the electrolysis apparatus comprising a liquid-retaining vessel, a cathode, an anode, and a collector between a lower portion of the cathode and the vessel;
 - 10 exposing the first tantalum-containing composition to a current within the electrolysis apparatus to electrolytically separate tantalum from other components of the first tantalum-containing composition;
 - collecting the separated tantalum in the collector; and
 - removing the collected tantalum from the electrolysis apparatus as a product material, the product material having tantalum therein at a second purity
 - 15 level which is higher than the first purity level.
2. The method of claim 1 wherein the product material has salts entrained therein; and further comprising, after removing the collected tantalum from the electrolysis apparatus as the product material:
 - 20 removing the entrained salts from the product material; and
 - after removing the entrained salts, e-beam melting of the product material.

3. The method of claim 1 wherein the product material has salts entrained therein; and further comprising, after removing the collected tantalum from the electrolysis apparatus as the product material:
- 5 removing the entrained salts from the product material by solvent extraction; and
- after removing the entrained salts, e-beam melting of the product material to increase the tantalum purity of the product material.
4. The method of claim 1 wherein the first tantalum-containing composition
- 10 comprises one or more of K_2TaF_7 , $TaCl_5$ and Ta_2O_5 .
5. The method of claim 1 wherein the first tantalum-containing composition comprises Ta in one or more compounds with one or more of F, Cl, Br and I.
- 15 6. The method of claim 1 wherein the first tantalum-containing composition comprises Ta in one or more compounds with O.
7. The method of claim 1 wherein the collector comprises a conductive material and is electrically connected with the cathode.
- 20 8. The method of claim 1 further comprising:
- providing a liquid electrolyte within the liquid-retaining vessel; and
- melting the first tantalum-containing composition within the liquid electrolyte prior to the electrolytic separation of tantalum from other
- 25 components of the tantalum-containing composition.

9. The method of claim 8 wherein the providing the first tantalum-containing composition comprises continuously feeding the first tantalum-containing composition into the liquid electrolyte during the collection of the separated tantalum in the collector.

5

10. The method of claim 8 wherein the providing the first tantalum-containing composition comprises intermittently feeding the first tantalum-containing composition into the liquid electrolyte during the collection of the separated tantalum in the collector.

10

11. The method of claim 1 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the providing the first tantalum-containing composition comprises feeding the first tantalum-containing composition into the basket.

15

12. The method of claim 11 wherein the feeding the first tantalum-containing composition into the basket occurs continuously during the collection of the separated tantalum in the collector.

20

13. The method of claim 11 wherein the feeding the first tantalum-containing composition into the basket occurs intermittently during the collection of the separated tantalum in the collector.

25

14. The method of claim 1 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the collector comprises a conductive material and is electrically connected with the cathode.

15. The method of claim 1 wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.
- 5 16. The method of claim 1 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.
- 10 17. The method of claim 1 wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum.
18. The method of claim 1 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the collector comprises one or more of
- 15 tantalum, nickel, cobalt and molybdenum.
19. A method of increasing tantalum purity, comprising:
- providing a starting composition, the composition including a compound that comprises tantalum and a halogen;
- 20 placing the composition within an electrolysis apparatus as a solution; the electrolysis apparatus comprising a liquid-retaining vessel, a cathode, an anode, and a collector between a lower portion of the cathode and the vessel;
- exposing the compound to a current within the electrolysis apparatus to electrolytically separate the tantalum from the halogen;
- 25 collecting the separated tantalum in the collector; and
- removing the collected tantalum from the electrolysis apparatus as a product material, the product material having a higher tantalum purity than the starting composition.

20. The method of claim 19 wherein the solution within the electrolysis apparatus is non-aqueous.
- 5 21. The method of claim 19 wherein the halogen is fluorine.
22. The method of claim 19 wherein the compound is K_2TaF_7 .
- 10 23. The method of claim 19 wherein the solution within the electrolysis apparatus comprises a molten mixture which includes one or both of NaCl and KCl; and wherein the compound is K_2TaF_7 .
24. The method of claim 19 wherein the collector comprises a conductive material and is electrically connected with the cathode.
- 15 25. The method of claim 19 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the collector comprises a conductive material and is electrically connected with the cathode.
- 20 26. The method of claim 19 wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.
- 25 27. The method of claim 19 wherein the collector is shaped as a basket surrounding a lower portion of the cathode; and wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.

28. The method of claim 19 wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum.
29. The method of claim 19 wherein the collector is shaped as a basket surrounding
5 a lower portion of the cathode; and wherein the collector comprises one or more of tantalum, nickel, cobalt and molybdenum.
30. The method of claim 19 wherein the collector consists essentially of tantalum.
- 10 31. The method of claim 19 wherein the collector is shaped as a basket surrounding a lower portion of the cathode, and wherein the collector consists essentially of tantalum.
32. The method of claim 19 wherein the anode comprises graphite and has a surface
15 exposed to the solution within the electrolysis apparatus, and further comprising providing a source of oxygen within the solution to react with the graphite of the anode at the surface and expose a fresh surface of the graphite to the solution.
33. The method of claim 32 wherein the source of oxygen consists essentially of
20 tantalum oxide.
34. The method of claim 32 wherein the solution within the electrolysis apparatus
comprises a molten mixture which includes one or both of NaCl and KCl; wherein the
compound is K_2TaF_7 ; and wherein the source of oxygen consists essentially of
25 tantalum oxide.
35. The method of claim 19 wherein the removing the collected tantalum comprises lifting the collector out of the solution.

36. The method of claim 19 wherein the collector is shaped as a basket surrounding a lower portion of the cathode, and wherein the removing the collected tantalum comprises lifting the collector out of the solution.

5

37. The method of claim 19 wherein the removing the collected tantalum does not comprise lifting the collector out of the solution.

10 38. The method of claim 19 wherein the collector is shaped as a basket surrounding a lower portion of the cathode, and wherein the removing the collected tantalum does not comprise lifting the collector out of the solution.

39. An electrolysis apparatus for producing tantalum, comprising:

a liquid-retaining vessel;

15

a tantalum-comprising liquid within the vessel;

a cathode extending into the tantalum-comprising liquid within the vessel;

a tantalum-collector positioned between a lower portion of the cathode and the vessel;

an anode contacting the liquid;

20

a power source providing an electrical current between the anode and cathode, and defining a circuit comprising the liquid, anode and cathode.

40. The apparatus of claim 39 wherein the vessel comprises a sidewall in contact with the liquid, and wherein the sidewall is the anode.

25

41. The apparatus of claim 39 wherein the vessel comprises a graphite material.

42. The apparatus of claim 39 wherein the vessel comprises a graphite inner material retained within an iron outer material, and wherein the liquid contacts the inner material and not the outer material.
- 5 43. The apparatus of claim 39 wherein the vessel comprises a graphite inner material retained within an iron outer material; wherein the liquid contacts the inner material and not the outer material; and wherein the anode comprises at least one carbon-containing rod extending into the liquid.
- 10 44. The apparatus of claim 39 wherein the vessel comprises a graphite inner material retained within an iron outer material, wherein the liquid contacts the inner material and not the outer material; and further comprising a graphite lid over the liquid and supported by the graphite inner material.
- 15 45. The apparatus of claim 39 wherein
the vessel comprises a graphite inner material retained within an iron outer material;
the liquid contacts the graphite inner material and not the iron outer material;
20 the graphite inner material comprises a sidewall in contact with the liquid;
and
the sidewall is the anode.
- 25 46. The apparatus of claim 45 further comprising a graphite lid over the liquid and supported by the graphite inner material.
47. The apparatus of claim 39 wherein the vessel comprises a ceramic material.



48. The apparatus of claim 39 wherein the cathode comprises a tantalum-comprising material within the liquid.
49. The apparatus of claim 39 wherein the cathode is comprised by a member
5. extending from above the liquid to within the liquid; the member having a first portion above the liquid and a second portion within the liquid; and the first portion having a different composition than the second portion.
50. The apparatus of claim 49 wherein the first portion predominately comprises
10 nickel; and wherein the second portion predominately comprises tantalum.
51. The apparatus of claim 39 wherein the tantalum-collector is a basket.
52. The apparatus of claim 51 wherein the basket comprises a conductive material
15 and is electrically connected with the cathode.
53. The apparatus of claim 51 wherein the basket comprises one or more of tantalum, nickel, cobalt and molybdenum.
- 20 54. The apparatus of claim 51 wherein the basket comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.
55. The apparatus of claim 51 wherein the basket consists essentially of tantalum.
25
56. The apparatus of claim 39 wherein the tantalum-collector is a basket, and is only partially submerged in the liquid.

57. The apparatus of claim 39 wherein the tantalum-collector comprises a conductive material and is electrically connected with the cathode.

58. The apparatus of claim 39 wherein the tantalum-collector comprises one or more of tantalum, nickel, cobalt and molybdenum.

59. The apparatus of claim 39 wherein the tantalum-collector comprises one or more of tantalum, nickel, cobalt and molybdenum, and is electrically isolated from the cathode.

60. The apparatus of claim 39 wherein the tantalum-collector consists essentially of tantalum.

61. A high purity tantalum material comprising at least 99% tantalum, by weight, and less than 3 ppm nitrogen.

62. The high purity tantalum material of claim 61 comprising at least 99.95% tantalum.

63. The high purity tantalum material of claim 61 comprising at least 99.995% tantalum.

64. The high purity tantalum material of claim 61 comprising less than or equal to 1.5 ppm nitrogen.

65. The high purity tantalum material of claim 61 comprising less than 15 ppm oxygen.

66. The high purity tantalum material of claim 61 comprising less than or equal to 12 ppm oxygen, and less than or equal to 1.5 ppm nitrogen.

67. The high purity tantalum material of claim 61 being in a shape of a physical
5 vapor deposition target.

ABSTRACT OF THE DISCLOSURE

The invention encompasses an electrolytic method of increasing tantalum purity, and an electrolysis apparatus that can be utilized in methodology for producing tantalum. The invention also encompasses a high purity tantalum compositions.

5

1 TANTALUM SPUTTERING TARGET AND METHOD OF MANUFACTURE

US 6,323,055 filing date
05/21/99

FIELD OF THE INVENTION

5 This invention relates to a method and apparatus for producing high purity tantalum and the high purity tantalum so produced. In particular, the invention relates to production of high purity tantalum.

BACKGROUND OF THE INVENTION

10 Tantalum is currently used extensively in the electronics industry which employs tantalum in the manufacture of highly effective electronic capacitors. This is mainly attributed to the strong and stable dielectric properties of the oxide film on the anodized metal. Both wrought thin foils and powders are used to manufacture bulk capacitors. In addition, thin film capacitors for microcircuit applications are formed by anodization of tantalum films, which are normally produced by sputtering. Tantalum is also sputtered in
15 an Ar-N₂ ambient to form an ultra thin TaN layer which is used as a diffusion barrier between a Cu layer and a silicon substrate in new generation chips to ensure that the cross section of the interconnects can make use of the high conductivity properties of Cu. It is reported that the microstructure and stoichiometry of the TaN film are, unlike TiN, relatively insensitive to the deposition conditions. Therefore, TaN is considered a much
20 better diffusion barrier than TiN for chip manufacture using copper as metallization material. For these thin film applications in the microelectronics industry, high purity tantalum sputtering targets are needed.

Most of the tantalum metal produced in the world today is derived from sodium reduction of potassium heptafluotantalate (K₂TaF₇). Processes which are not adapted
25 commercially to any significant extent include the reduction of tantalum oxide (Ta₂O₅) with metallic reductants such as calcium and aluminum, and non metallic reductants carbon and carbon nitrogen; the reduction of the tantalum pentachloride (TaCl₅) with magnesium, sodium or hydrogen; and the thermal dissociation of TaCl₅.

30 Reduced tantalum is obtained either as powder, sponge or massive metal. It invariably contains significant amounts of oxygen, as well as other impurities such as reductants and impurities that may be present in the starting tantalum compounds. For removal of impurities in tantalum, electron beam melting is often conducted. During electron beam melting, most of the metallic impurities and interstitial gases are vaporized because of their high vapor pressure at the melting point of tantalum (2996°C).

35 Essentially all elements, except niobium, tungsten, molybdenum, uranium and thorium can

1 be eliminated this way. While the metallic impurities and nitrogen are removed by direct
volatilization, the removal of oxygen takes place via mechanisms involving formation and
evaporation of carbon oxides, aluminum oxides, water, as well as suboxides of tantalum.
The purity can be further improved by repeated electron beam melting. Other refining
5 processes include vacuum arc melting, vacuum sintering, molten salt electrorefining and
tantalum iodide refining, with the iodide process being the most promising technique for
removing tungsten and molybdenum.

The above mentioned refining methods are not effective for removal of niobium
from tantalum. Since tantalum and niobium are closely associated with each other in
10 nature, the removal of niobium is critical to prepare very high pure tantalum. In practice,
their separation is conducted before reduction via methods such as solvent extraction,
chlorination and fractional crystallization.

The tantalum target manufacturing process includes forging ingot into billet, surface
machining billet, cutting billet into pieces, cold rolling the pieces into blanks, annealing
15 blanks, final finishing and bonding to backing plates.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a method and apparatus
for producing high purity tantalum sputtering targets and the high purity tantalum so
20 produced.

The method comprises purifying potassium heptafluorotantalate, K_2TaF_7 , reducing the
purified K_2TaF_7 to produce tantalum powder, refining the tantalum by reacting with iodine
and finally electron beam melting the tantalum to form a high purity tantalum ingot.

The starting material is commercial K_2TaF_7 salt, made by dissolving tantalum ores
25 in hydrofluoric and sulfuric acid mixture, followed by filtration, solvent extraction using
methkylisobutylketone (MIBK) and crystallization of K_2TaF_7 . This can be repeated several
times to lower the impurity levels, in particular the level of Nb.

Sodium reduction of purified K_2TaF_7 is conducted in a liquid liquid reduction retort
where K_2TaF_7 and diluents (KCl and NaCl) are heated to about 1000°C. Molten sodium
30 is then injected into the retort for reacting with K_2TaF_7 . Agitation of the reactants is
provided to accelerate the reduction reaction. After cooling, the mass is taken out of the
retort, crushed, leached and washed to separate tantalum powder from the salt mixture.

Tantalum refining is done by the iodide process or electron beam melting. These
methods can be used in parallel or in series. Electron beam melting is preferred as the last
35

1 step because it results in an ingot which is suitable for further physical metallurgical steps
toward the goal of target manufacture.

5 Electron beam melted ingot is forged into billets and surface machined. After
surface machining, the forged billet is cut into pieces, which are further cold rolled into
blanks. Blank annealing is carried out in an inert atmosphere to obtain a recrystallized
microstructure. The blanks are then machined to obtain a final finish and bonded to
copper or aluminum backing plates.

10 For characterization of targets produced by the invented process, chemical analyses
are conducted. The methods of chemical analysis used to derive the chemical descriptions
set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for
metallic elements and LECO gas analyzer for non metallic elements.

15 The highly purified tantalum material of the present invention has less than 500
ppm by weight, total metallic impurities, an oxygen content of less than about 100 ppm,
by weight, a molybdenum or tungsten content of not more than 50 ppm, by weight, and a
uranium and thorium content of not more than 10 ppb, by weight. It is also possible to
produce tantalum having less than 5 ppm, by weight, total of molybdenum and tungsten.

1 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of the liquid liquid reaction retort used for sodium reduction of K_2TaF_7 ;

Figure 2 is a schematic diagram of an iodide cell;

5 Figure 3 is a schematic diagram illustration an iodide cell with a distillation unit;

Figure 4A and 4B are schematic diagrams of a tantalum target; and

Figure 5 is a graph of conductance of tantalum bar as a function of time.

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1 DETAILED DESCRIPTION

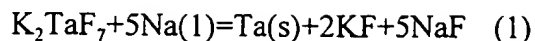
1) Precursor Purification and Sodium Reduction

In nature, tantalum generally occurs in close association with niobium, tin and other elements. The minerals most commonly used as raw materials in tantalum production are
5 Tantalite, Wodginite, Micolite and Samarskite. These minerals are enriched by wet gravity, magnetic or electrostatic methods. The concentrates are dissolved in a mixture of hydrofluoric and sulfuric acid. The resulting solution is filtered, then separated from niobium and other impurities in a solvent extraction plant. The tantalum concentrate is transferred into an aqueous solution and precipitated with ammonia to yield tantalum acid
10 ($\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), calcined at an elevated temperature to yield tantalum oxide. Alternatively, the tantalum is crystallized to potassium heptafluorotantalate, by addition of KF and KCl to the hot aqueous solution obtained from solvent extraction. Impure potassium heptafluorotantalate obtained by these methods must be further purified for use as a source of tantalum for the electronics industry.

15 In general, potassium heptafluorotantalate may be purified by a procedure such as follows:

Technical grade potassium heptafluorotantalate (K_2TaF_7) is dissolved in HF, e.g. a 49% HF solution. A mixture of HF and H_2SO_4 can also be used for the dissolution process. The amount of K_2TaF_7 dissolved depends on the temperature and
20 concentration of HF. Since the dissolution rate is very slow at room temperature, the mixture is heated e.g. to 90°C in a suitable container. The solution containing K_2TaF_7 is covered, to prevent losses due to evaporation, and stirred continuously. Time to dissolution is approximately one hour. A 65°C KCl solution is added to the K_2TaF_7 solution and the resulting solution is stirred while cooling to room temperature. The
25 tantalum in solution precipitates as K_2TaF_7 since the solubility of K_2TaF_7 is very low at room temperature. The precipitate is filtered, washed and dried. Niobium, tungsten, molybdenum, zirconium, uranium and thorium remain in solution. Repeated dissolution and precipitation may be useful in order to obtain extremely high purity tantalum. Elements such as niobium, tungsten, molybdenum, uranium and thorium, which are
30 difficult to remove by electron beam melting, are easily removed by this process.

Potassium heptafluorotantalate can be reduced to tantalum metal by fused salt electrolysis or reduction by sodium. The rate of reduction by electrolysis is very slow, therefore sodium reduction is used for processing large quantities of K_2TaF_7 into tantalum metal. The overall reduction reaction can be written as

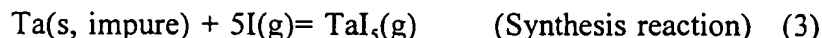
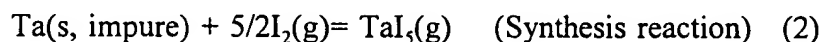


Referring to the drawings, FIG. 1 shows a reduction furnace. The reduction is carried out by placing K_2TaF_7 and some dilute salts such as KCl , NaCl , LiCl , CsCl , CaCl_2 , etc. into a reactor equipped with a stirring device. The reactor is placed in a furnace heated to above the melting point of the salt mixture, usually under 1000°C . Molten sodium is injected into the reactor and stirred while controlling the temperature. After cooling, the mass is removed from the reactor, crushed and leached with a dilute acid to recover tantalum metal powder. The powder is compacted and melted in an electron beam furnace.

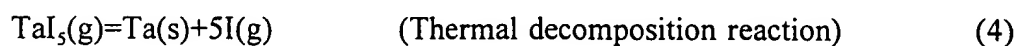
2) Iodide Process

Tantalum metal is produced from the reduction of commercially available K_2TaF_7 by sodium, which is a process similar to the Hunter process used for the production of sponge titanium. The metal produced by the reduction of sodium contains most of the impurities that exist in the K_2TaF_7 , such as Fe , Ni , Ti , W , Mo , etc. The metal is in the form of powder and has a very high oxygen content.

The method described herein is capable of producing high purity tantalum from scrap or impure tantalum metal. The process is based on chemical transport reactions, in which tantalum iodides are formed by the reaction of impure tantalum metal with iodine gas (synthesis zone), at lower temperatures, then the tantalum iodides are decomposed on a hot wire filament, at higher temperatures, to produce a very pure metal (deposition or thermal decomposition zone.). The impure tantalum is converted into gaseous species according to the following reactions in the synthesis zone:



Similar reactions can be written for the other tantalum iodide species, such as TaI_3 and TaI_2 . The gaseous species of tantalum diffuse into the thermal decomposition zone and decompose to form pure tantalum metal according to the following reaction:



1 The thermodynamic factors are important to understanding and controlling the
process. Thermodynamic calculations have been carried out to determine advantageous
operating conditions, such as temperature and pressure, in the synthesis and decomposition
zones.

5 A schematic diagram of the apparatus is shown in Figure 2. The process apparatus
contains a cell, filament and feed material and is designed to run batch operations. After
each run the apparatus is cooled to room temperature and disassembled.

10 The preferred iodide cell, for the refining of tantalum, is an alloy 600 (Inconel)
container clad with a metal more electrochemically noble than tantalum according to the
chloride electromotive series, such as molybdenum or tungsten or an alloy thereof. The
cladding prevents contamination of the refined tantalum by cell components since
molybdenum and tungsten do not react with iodine at cell operating temperatures. Alloy
600 (Inconel) containers are also used for the refining of metals such as Ti and Zr, without
cladding, since these metals are refined under different operating conditions.

15 A filament made of pure tantalum rod is used for the decomposition surface. The
filament can be in the shape of a U or can be a different shape to increase its surface area.
It is also possible to use multiple filaments to increase the surface area and cell
productivity. The filament is heated resistively by an external power supply. Since the
filament temperature affects the deposition rate, the current is controlled to maintain the
20 filament temperature between 1000 and 1500°C. Tantalum crystals then grow on the
filament.

25 A cylindrical molybdenum screen is placed in the cell to provide an annular space
1 to 3 inches wide. The annular space is filled with tantalum feed material in the form of
chips, chunks or small pellets. This type of arrangement gives a high surface area for the
reaction between feed material and iodine gas in the cell. The crude tantalum can also be
compacted to a donut shape and placed in the reactor. The feed materials are cleaned with
cleaning agents before they are charged into the cell.

30 A good vacuum system is advantageous to producing tantalum with low impurities.
Therefore, the cell is connected to a vacuum system producing 1 micron or less of
pressure. The cell is evacuated at room temperature, then heated to around 800-1000°C
under vacuum to remove all the volatile impurities before iodine is added.

35 The temperature in the synthesis zone effects the rate of reaction. The temperature
in the synthesis zone should be uniform and kept much higher than boiling point of TaI_5 .
A special heater placed on the lid of the cell keeps the temperature at around 350-500°C,

1 which prevents the condensation of iodides under the lid. Without this heater, iodine must
be continuously added to the system.

Oxygen in tantalum originates from numerous sources, starting with the precursor
and on through electron beam melting. Oxygen is undesirable at high concentrations due
5 to its effect on the resistivity of deposited tantalum thin films. Currently available
methods cannot easily decrease the oxygen levels to less than 30 ppm. Thermodynamic
calculations, as well as the experimental results, indicate that the metal oxides formed or
present in the feed material do not react with iodine and are not transported to the
decomposition zone. Therefore, this process is capable of producing high purity tantalum
10 with very low oxygen. The amount of oxygen remaining in the cell atmosphere is reduced
by a combination of argon flushing and vacuum. Nitrogen in the feed material behaves
like oxygen, therefore the nitrogen content of tantalum crystal bar will be very low.

Electron beam melting is frequently used to refine tantalum. However, electron
beam melting cannot remove elements such as tungsten and molybdenum, since the vapor
15 pressures of these elements are very low at the melting temperature of tantalum. The
present process is capable of consistently removing elements such as tungsten and
molybdenum to extremely low levels. The process may also remove uranium and thorium,
which cannot be removed by electron beam melting.

The iodide process described above may not be able to remove significant amounts
20 of niobium. Therefore, the current process has been modified to obtain pure tantalum with
very low metallic impurities including niobium. In the modified process, tantalum scrap
or crude tantalum is reacted with iodine gas to form gaseous TaI_5 and NbI_5 , which then are
separated by fractional distillation, since the boiling points of these two compounds are
different. A schematic of the apparatus is shown in Figure 3.

25 Crude tantalum or scrap is placed in a vertical tube made of Inconel and clad with
molybdenum, tungsten or an alloy thereof. The tube is placed in a furnace that is heated
to 400-700°C. A carrier gas such as clean argon or helium is passed over an iodine bath.
The temperature of the bath is adjusted to get a specific I_2 partial pressure. Iodine gas
reacts with tantalum scrap to produce gaseous tantalum and niobium iodide. The gas from
30 the feed reactor passes through the distillation columns. The temperature of the first
column is maintained just below the boiling point of TaI_5 , to condense TaI_5 . The second
column is maintained at a temperature low enough to condense NbI_5 , but above the boiling
point of I_2 . The iodine gas is circulated through the process of reuse. All the gas lines
between the first column and furnace are made of molybdenum and maintained at about
35 600°C, the others are maintained at lower temperatures.

1 The pure liquid or solid TaI_5 obtained from the fractional distillation unit is fed
into the deposition reactor and the TaI_5 decomposes on a hot surface to produce pure
tantalum crystals. Tantalum obtained from this process is very pure and free of all
impurities that cannot be removed by conventional processes. The pure tantalum obtained
5 by the modified iodide process is electron beam melted to produce high purity tantalum
ingots.

3. Electron Beam Melting

Electron beam melting is commonly used to melt and refine refractory materials.

10 The process is based on the use of the intense heat generated when a high energy
particle stream impinges on a material, transforming its kinetic energy into thermal energy.
The flexibility to distribute energy yields a large number of electron beam melting
techniques such as button, drip, hearth, zone melting, etc. for various metals. Electron
beam hearth melting has been established for titanium and super alloys. Electron beam
15 drip melting may be used for refractory materials. An electron beam drip melting furnace
comprises a horizontal bar feeder for primary feedstock. The bar feeder is equipped
with a vacuum valve which allows nearly continuous feeding and melting of precompacted
materials. The refining of refractory metals occurs via vaporization of suboxides,
evolution and removal of gases, carbon-oxygen reaction and vaporization of metallic
20 impurities. Most of the elements can be removed from tantalum during melting by the one
of above mechanisms. However, electron beam melting cannot remove W, Mo, Nb, U, Th,
etc. due to low vapor pressures of these elements at the melting temperature. Repeated
melting may be necessary to get very high purity materials.

25 Scrap, impure tantalum, tantalum powder obtained from electrolysis or reduction of
 K_2TaF_7 is compacted and melted in an electron beam drip melting furnace to produce high
purity tantalum ingots.

4. Target Manufacturing

30 Ingots obtained from electron beam melting are forged into billets and surface
machined. After surface machining, the forged billet is cut into pieces, which are further
cold-rolled into blanks. The blanks are annealed in an inert atmosphere to obtain the
desired microstructure. The blanks are then machined to obtain the final finish and may be
bonded to copper or aluminum backing plates. A schematic of the target produced is
shown in Figures 4A and 4B.

It is desirable to perform a chemical analysis and characterization of targets by measuring the grain size and texture. The methods of chemical analysis useful to derive the chemical descriptions set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for metallic elements and LECO gas analyzer for non-metallic elements. Line interception method is used for grain size determination and XRD and EBSP are used to obtain texture data.

EXAMPLE 1

About 350 grams of K_2TaF_7 was added to 595 cc of HF (49%) in a Teflon beaker. The mixture was heated to 90°C and stirred continuously. The beaker was covered with a Teflon plate to prevent evaporation of the solution. The dissolution process lasted about one hour. About 140 grams of KCl was dissolved in 700 cc of distilled water and heated to 60 C. The KCl solution was added to the K_2TaF_7 solution and the resulting solution was stirred for several minutes. The solution was cooled to room temperature which caused the tantalum in the solution to be precipitated as K_2TaF_7 , since the solubility of this compound is very low at room temperature. The precipitates were filtered and washed with KF solution (100 gr/liter H_2O) and distilled water. The powder was dried at 160°C in a vacuum furnace, then analyzed for composition. X-ray diffraction studies were carried out on the precipitates.

Several examples were carried out according the procedure described above and samples were analyzed. The niobium content of K_2TaF_7 was reduced by 50 percent after the first treatment. The results are shown in Table 1. The data shown in Table 1 indicates it is possible to decrease the niobium content of tantalum by this method. The purified K_2TaF_7 may be reduced by sodium.

Table 1

Element	Original K_2TaF_7	K_2TaF_7 , After First Wash	K_2TaF_7 , After Second Wash
Nb	4.6	<2.2	<1
Mo	0.2	0.1	0.1
W	4.8	1.1	<1
Zr	0.52	0.14	<0.1
Th	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01
Na	1100	130	50
Fe	4.8	1.2	<1
Al	2.5	1.2	
S	8.7	1.1	

1 The data in Table 1 has shown that the contents of Nb, Mo and W are largely
lowered by this method. It is well known that these elements cannot be removed from Ta
metal by electron beam melting. Therefore, a removal of these three elements from the
K₂TaF₇ is beneficial to producing very pure tantalum. Assuming all Nb, Mo and W in the
5 K₂TaF₇ will be co-reduced with Ta in the sodium reduction stage and neglecting the
existence of all other elements listed in Table 1, a simple calculation can be made to show
the influence of the K₂TaF₇ purification on metal purity. A complete sodium reduction of
1000 g of original K₂TaF₇ would produce 461.7 g of Ta which would contain 9.6 mg of
Nb, Mo and W, resulting in a metal purity of 99.9979%. When using 1000 g twice washed
10 K₂TaF₇, 461.7 g of Ta produced by sodium reduction would contain less than 2.1 mg of
Nb, Mo and W. The metal purity would then be 99.9995%.

EXAMPLE 2

15 An iodide cell was used to produce pure tantalum from scrap available in the
market. The cell was made of an Inconel alloy and lined with molybdenum for the
preliminary experiments. A molybdenum screen was placed inside the cell and Ta scrap
was used to fill the gap between the screen and the cell wall. The cell was leak checked,
then evacuated to below 10 microns. The cell was heated to 850 C, under vacuum, to
evaporate and remove organic and other volatile compounds. Then the cell was cooled to
20 room temperature and the precipitates on the lid were cleaned. A filament made of pure Ta
was installed on the cell lid. The cell was sealed and evacuated to below 10 microns again.
The feed was heated to about 500-600°C and the filament to 1000-1200 C. When the feed
and filament temperature were stabilized, a measured quantity of iodine crystals were
added to the reaction chamber. The current and voltage supplied to the filament were
25 measured continuously. From these values it is possible to calculate the conductance,
which is related to the diameter of the bar. The vessel pressure, and filament and feed
material temperatures were controlled. Tantalum bars are successfully grown by this
method.

30 It was found that the temperature of the filament and feed as well as the pressure
affects the deposition rate significantly. The growth rate of Ta bar is related to
conductance of Ta bar. The growth rate in terms of conductance (Mho) is shown in Figure
5. Very high deposition rates are obtained by this method as shown in Figure 5. Chemical
analyses of the resulting tantalum bars from several runs are given in Table 2. It must be
noted that scrap used in the experiments was not homogenous in composition. The original
35 composition of the tantalum feed material is also shown in Table 2.

Table 2

		Run 1	Run 2		Run 3	Run 4
Time, hrs		79	45		62	45
Weight, gr		5925	5043		7829	5969

Element (ppm)	Feed 1 & 2	Run 1	Run 2	Feed 3 & 4	Run 3	Run 4
Nb	1200	900	505	90	185	230
Mo	6	1.2	1.7		1.3	1.2
W	30,000	0.28	0.19		0.2	0.25
O	100	90	308	100	60	176
N	100	<10	3	100	6	4

EXAMPLE 3

Tantalum crystal bars from various runs were melted in an electron beam furnace. The analytical results of the tantalum feed stock and the melted tantalum ingot are shown in Table 3.

Table 3

Element	Feed Material Concentration (Average ppm)	Concentration After Melting (Average ppm)
Fe	344	1
Ni	223	0.13
Cr	205	0.19
Nb	463	270
O	221	<25

EXAMPLE 4

Ingots obtained from electron beam melting are cold worked and annealed to produce target blanks. Initial ingot breakdown is done via a combination of side and upset forging. After surface machining, the forged ingot is cut into pieces, which are further cold rolled into blanks. Two rolling temperatures are considered: room temperature and liquid nitrogen temperature. The former is called cold rolling, while the latter is referred to as cryogenic rolling. The reduction at rolling is in the range of 70 to 90%. The rolled blanks are annealed in an inert atmosphere or vacuum under different conditions to obtain the desired microstructure and texture.

1 EXAMPLE 5

Blanks with fine grains and desired texture are machined to obtain the final finish and bonded to copper or aluminum backing plates. A schematic of the target produced is shown in Figures 4A and 4B.

5 In the foregoing discussions, it is apparent that various changes and modifications may be made within the preview of the invention. Accordingly, the scope of the invention should be limited only by the appended claims.

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1 CLAIMS:

1. A method for producing high purity tantalum comprising the steps of:
purifying K_2TaF_7 by a dissolution process;
reacting purified K_2TaF_7 with a reducing agent to produce tantalum powder;
5 and
reacting said tantalum powder with iodine in a container.
2. A method according to claim 1, wherein HF or a mixture of HF and H_2SO_4
is used in the dissolution of K_2TaF_7 .
10
3. A method according to claim 1, wherein a solution containing KCl is used
to precipitate said K_2TaF_7 from the solution.
4. A method according to claim 1, wherein Nb and other metallic impurities in
15 said K_2TaF_7 are reduced to levels lower than about 20 ppm, by weight.
5. A method according to claim 1, wherein W and Mo in said K_2TaF_7 are
reduced to less than about 1 ppm, by weight.
- 20 6. A method according to claim 1, wherein said reducing agent is sodium.
7. A method according to claim 1, wherein said container has a reactant-
contacting surface comprising a metal more electrochemically noble than tantalum
according to the chloride electromotive series.
25
8. A method according to claim 7, wherein said reactant-contacting surface
comprises molybdenum, tungsten or an alloy of molybdenum and tungsten.
9. A method according to claim 1, further comprising electron beam melting
30 said tantalum to produce a high purity tantalum ingot.
10. A method for producing high purity tantalum comprising reacting impure
tantalum with iodine gas in a container and decomposing tantalum iodides on a filament.
35

1 11. A method according to claim 10 wherein said container has a reactant-
contacting surface comprising a metal more electrochemically noble than tantalum
according to the chloride electromotive series.

5 12. A method according to claim 11 wherein said reactant-contacting surface
comprises molybdenum, tungsten or an alloy of molybdenum and tungsten.

 13. A method according to claim 10 wherein said filament comprises tantalum.

10 14. A method according to claim 10 further comprising electron-beam melting
said tantalum to form a high-purity tantalum ingot.

 15. High purity tantalum comprising tantalum and less than about 500 ppm, by
weight, total metallic impurities.

15 16. High purity tantalum comprising less than about 50 ppm, by weight, tungsten
or molybdenum.

20 17. High purity tantalum comprising less than about 20 ppm, by weight, tungsten
or molybdenum.

 18. High purity tantalum comprising less than about 5 ppm, by weight, each of
tungsten and molybdenum.

25 19. High purity tantalum comprising less than 20 ppm, by weight, total of
niobium, molybdenum and tungsten.

 20. High purity tantalum comprising tantalum and less than 5 ppm, by weight,
total of niobium, molybdenum and tungsten.

30 21. A sputtering target comprising high purity titanium according to claim 15.

 22. A sputtering target comprising high purity titanium according to claim 16.

35 23. A sputtering target comprising high purity titanium according to claim 17.

- 1
24. A sputtering target comprising high purity titanium according to claim 18.
25. A sputtering target comprising high purity titanium according to claim 19.
- 5
26. A thin film produced by a sputtering target according to claim 15.
27. A thin film produced by a sputtering target according to claim 16.
- 10
28. A thin film produced by a sputtering target according to claim 17.
29. A thin film produced by a sputtering target according to claim 18.
- 15
30. A thin film produced by a sputtering target according to claim 19.
- 20
- 25
- 30
- 35

TANTALUM SPUTTERING TARGET AND METHOD OF MANUFACTURE

ABSTRACT OF THE DISCLOSURE

Described is a method for producing high purity tantalum, the high purity tantalum so produced and sputtering targets of high purity tantalum. The method involves purifying starting materials followed by subsequent refining into high purity tantalum.

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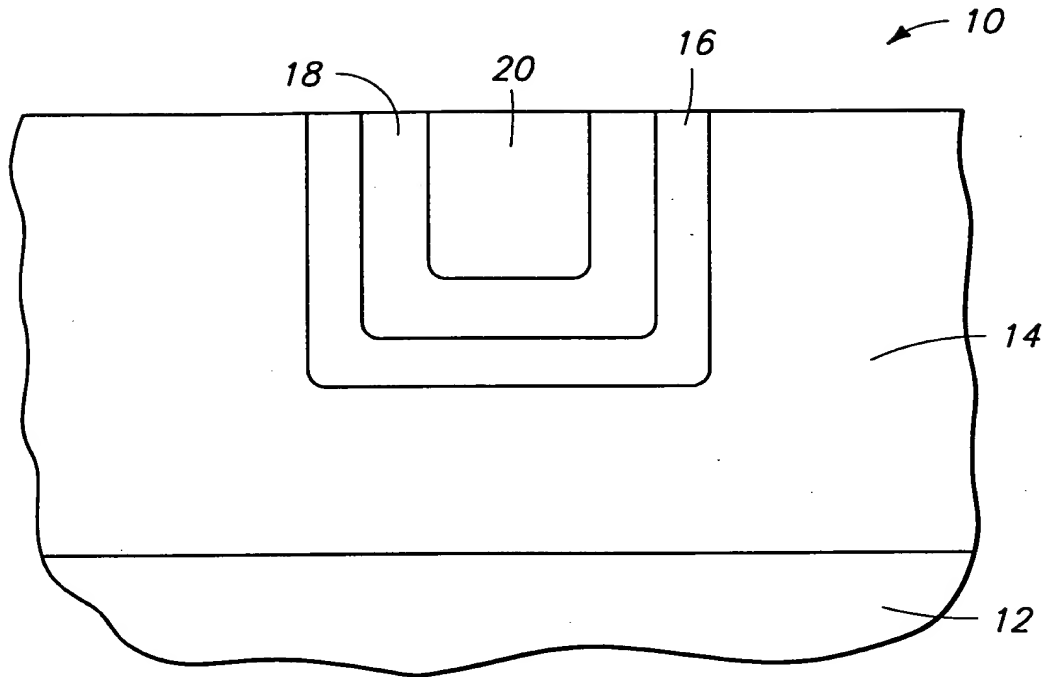


FIG. 1
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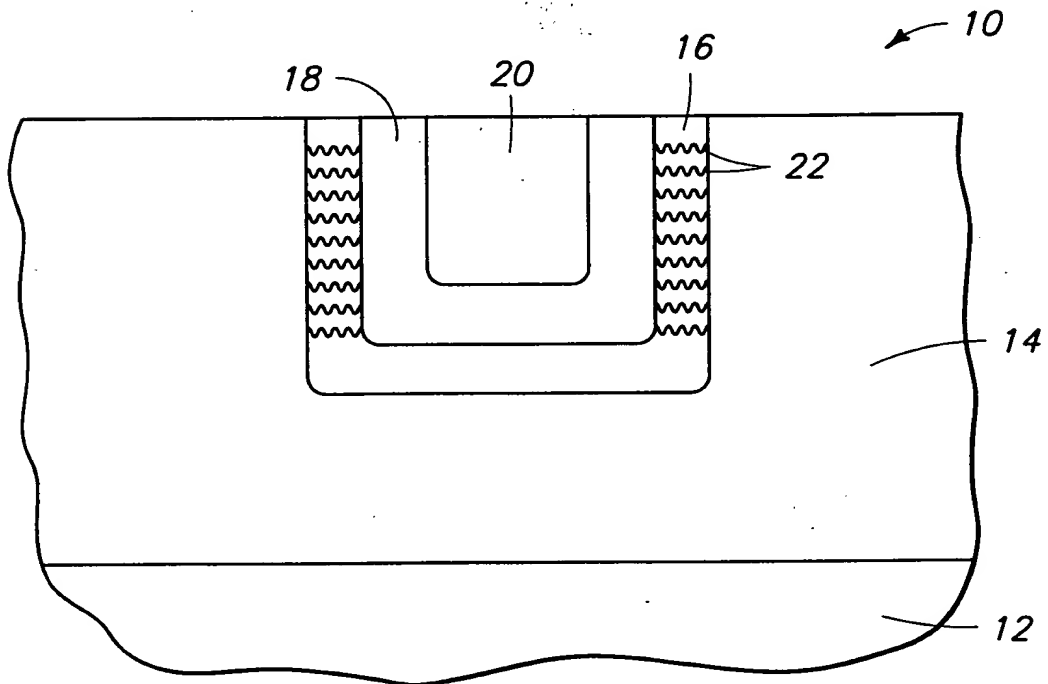
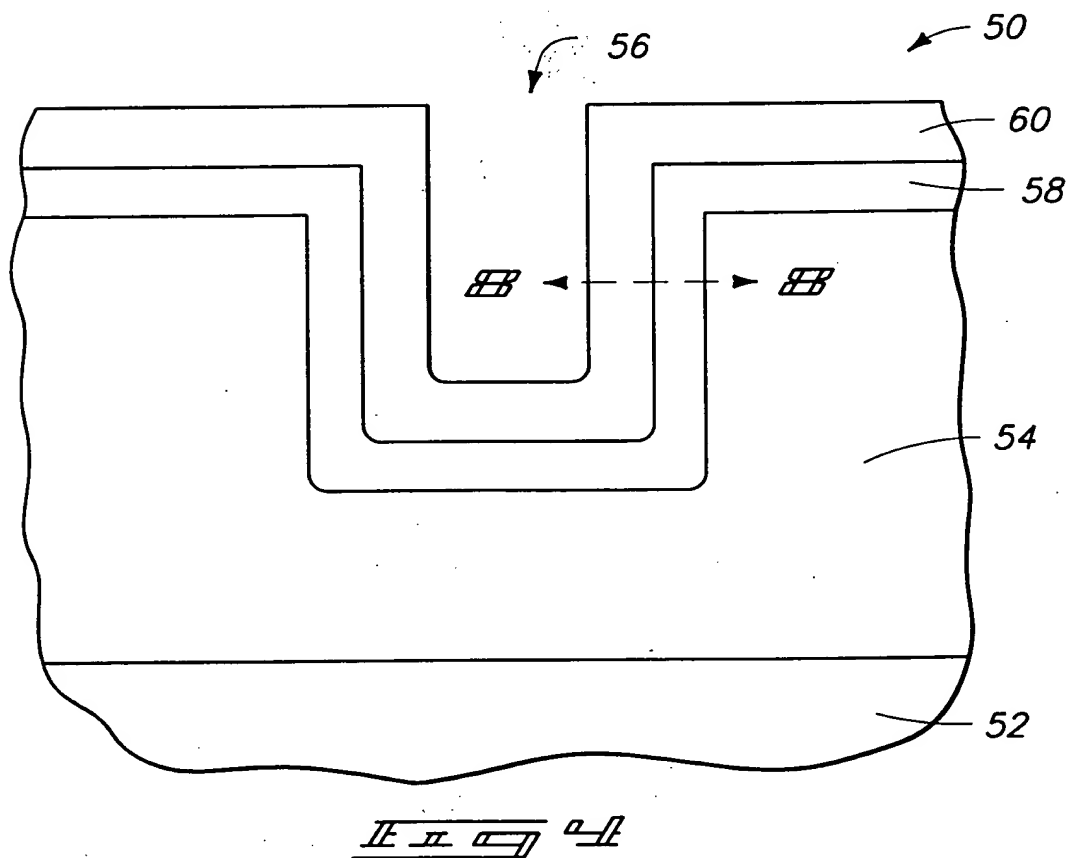
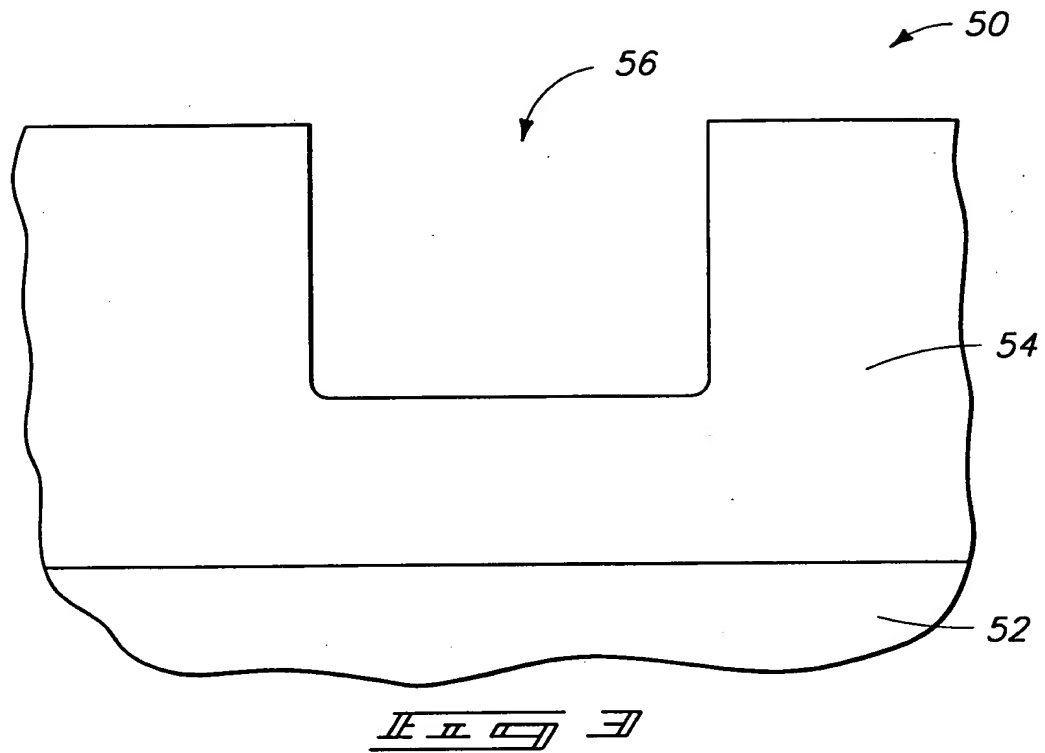
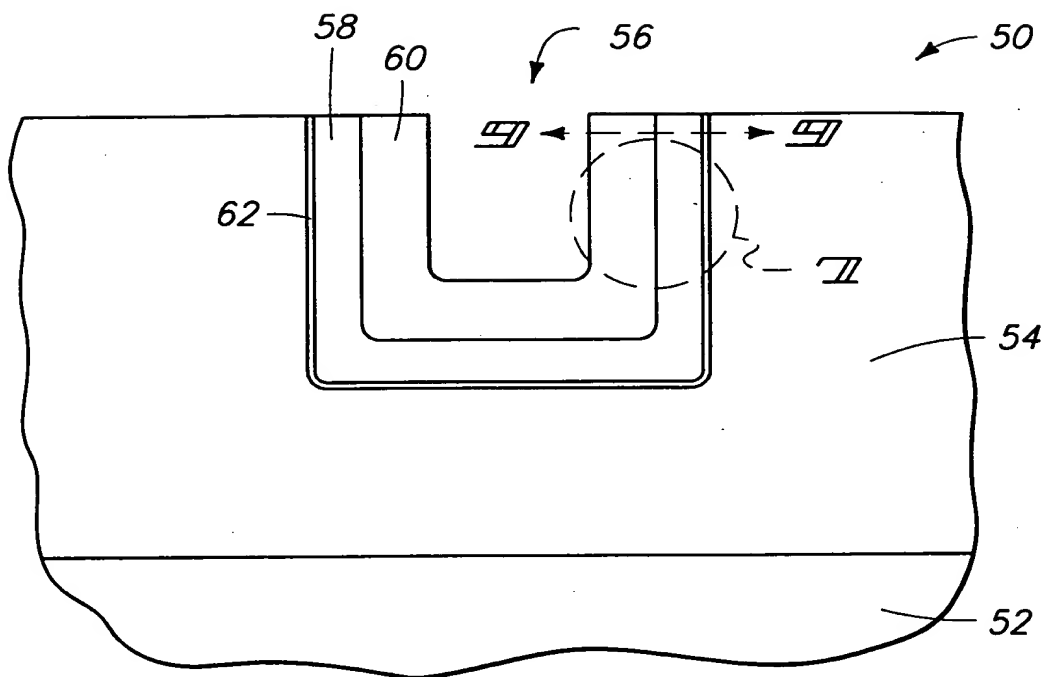


FIG. 2
PRIOR ART

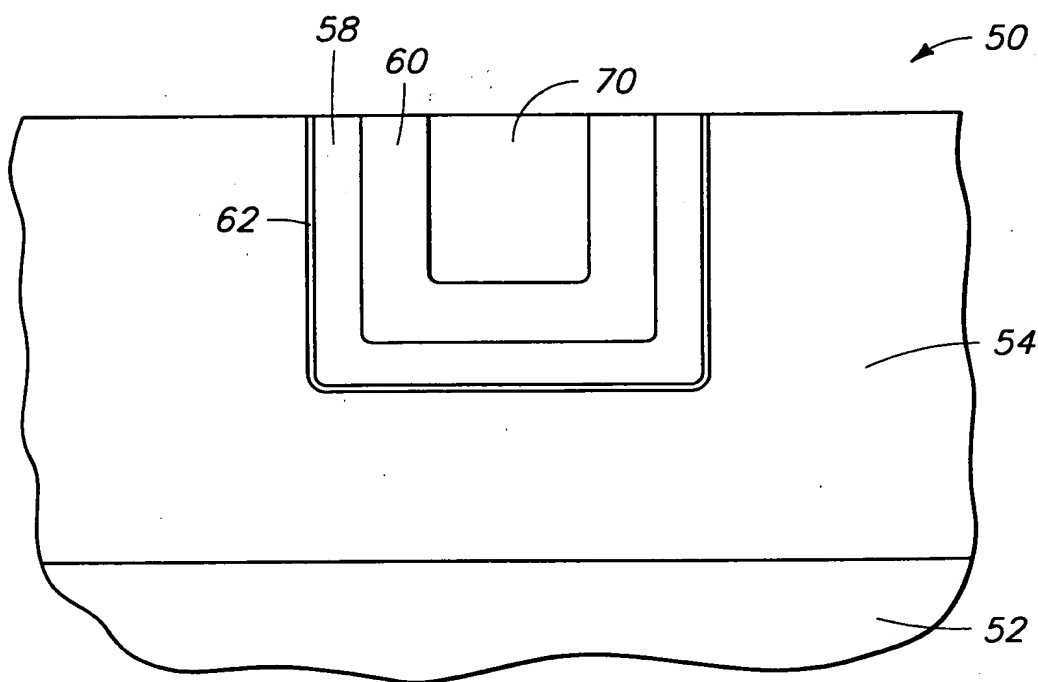
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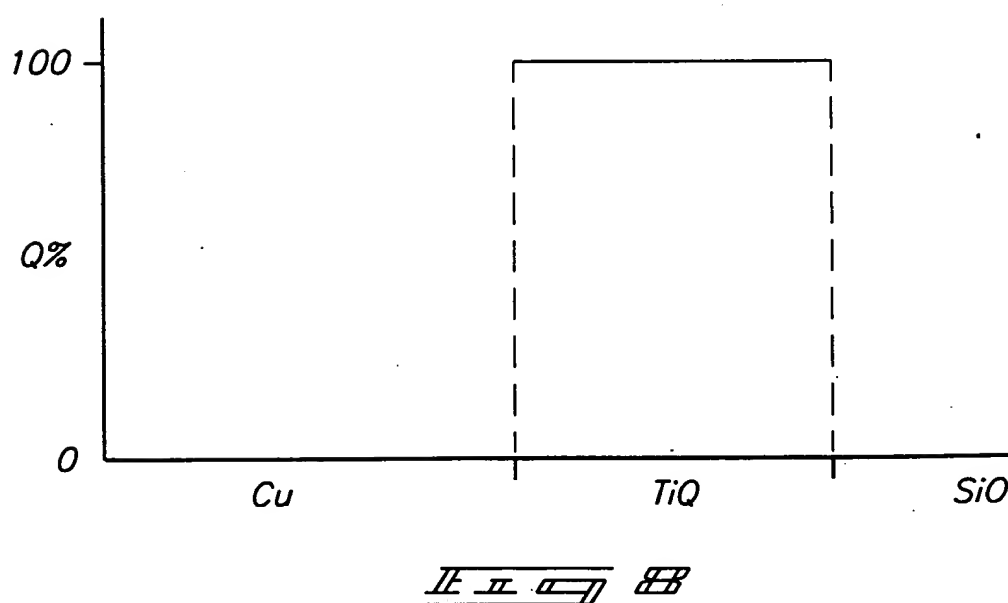
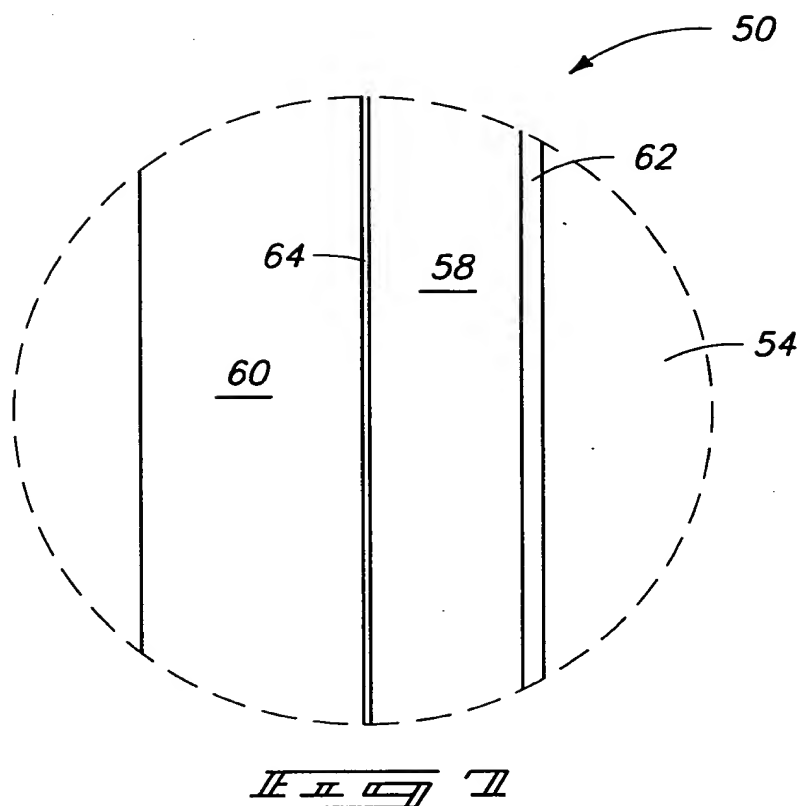


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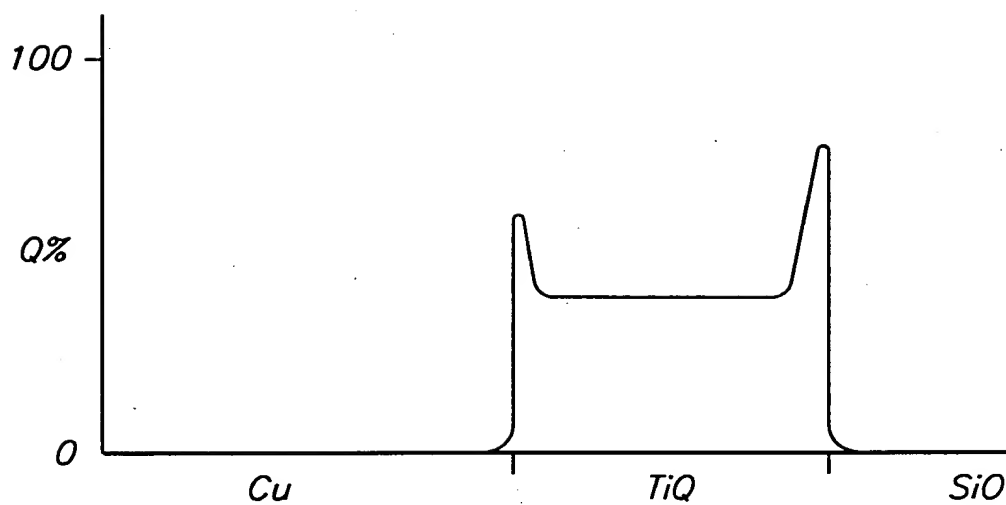


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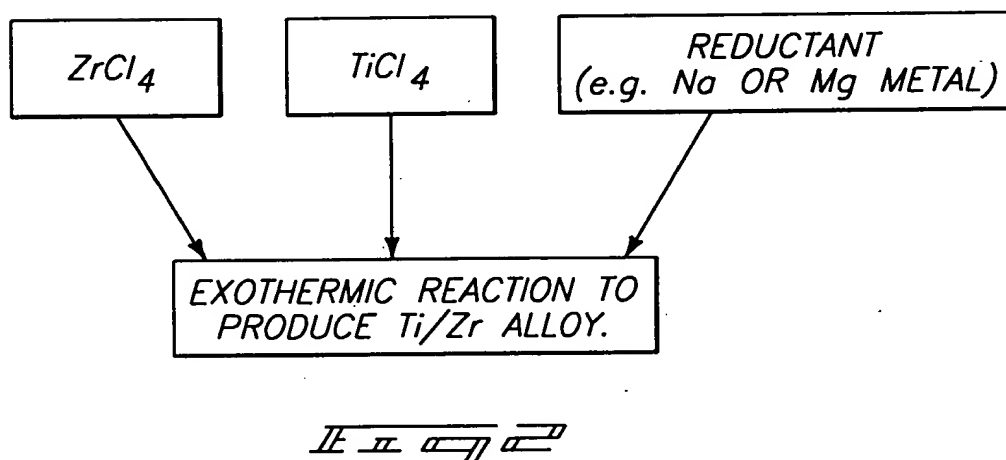
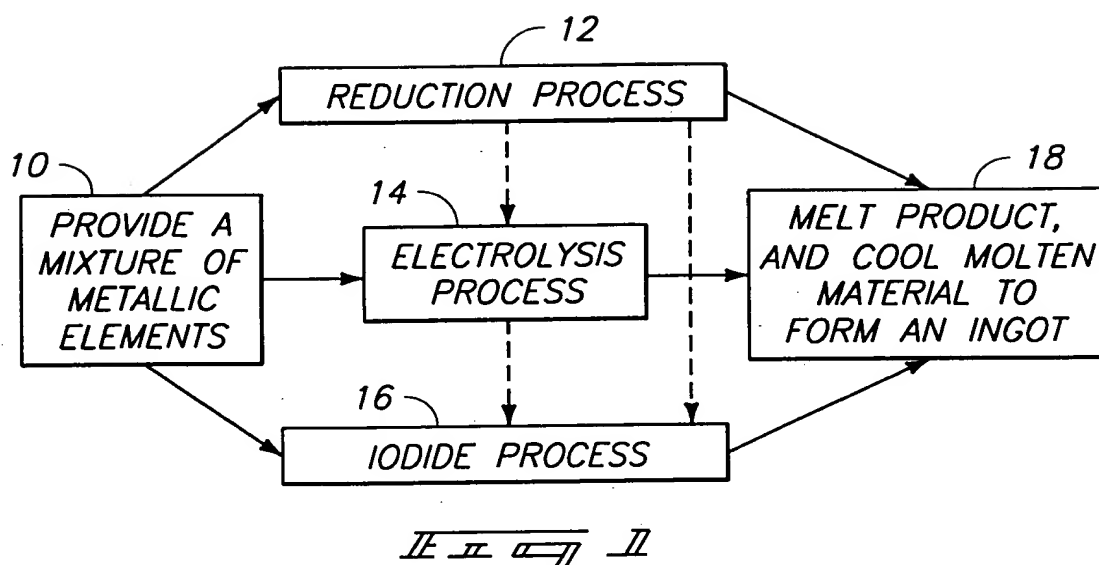


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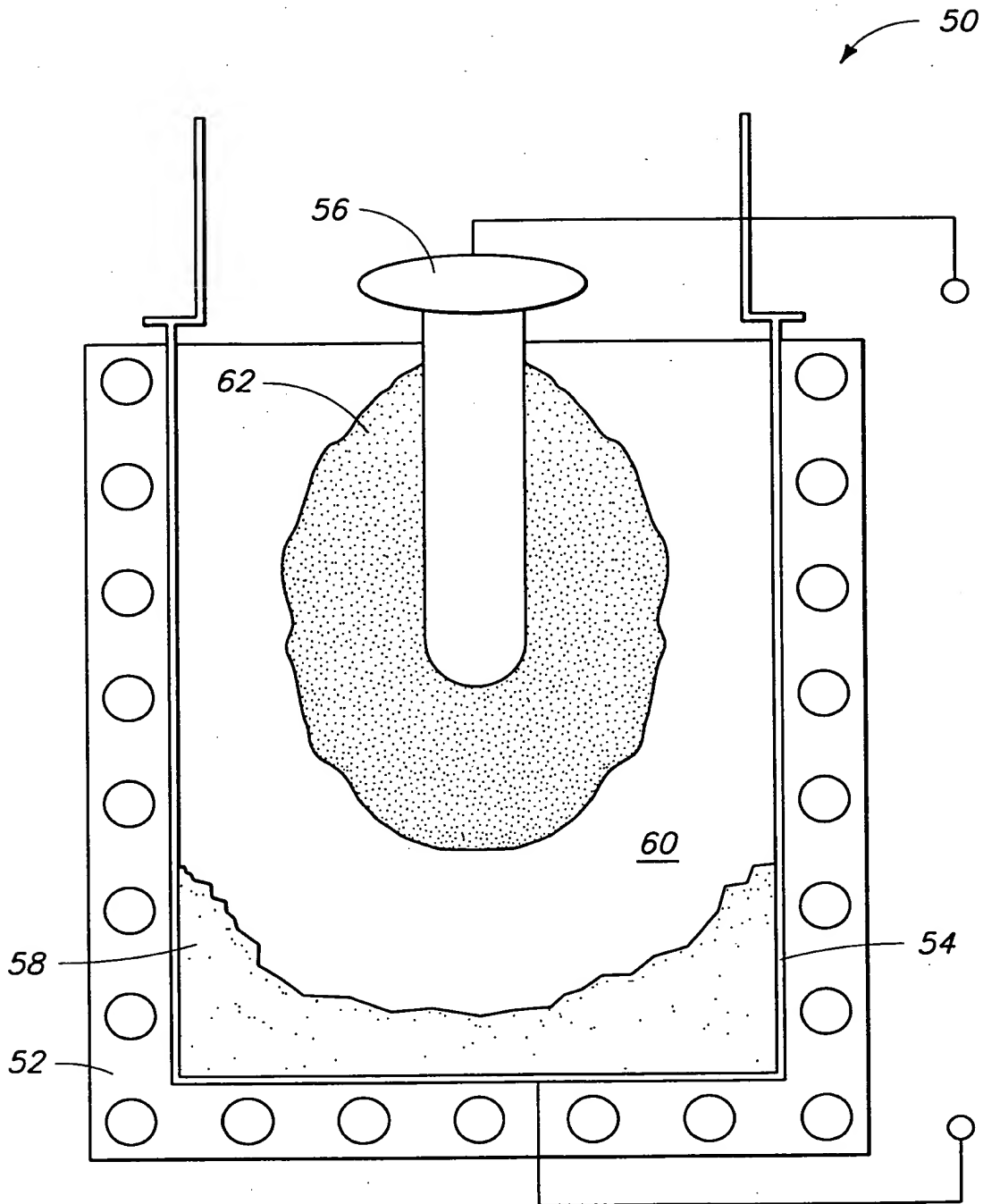
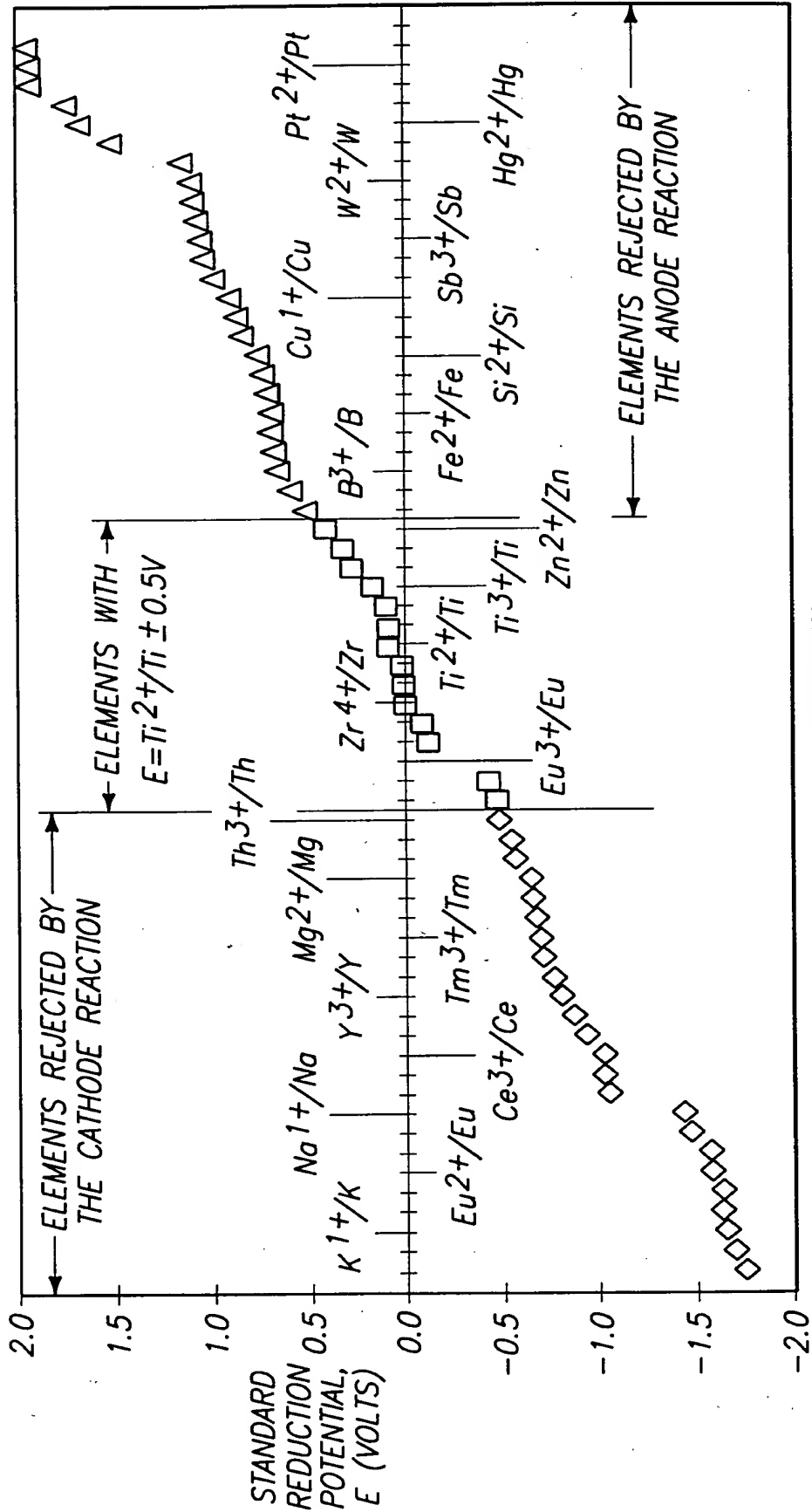


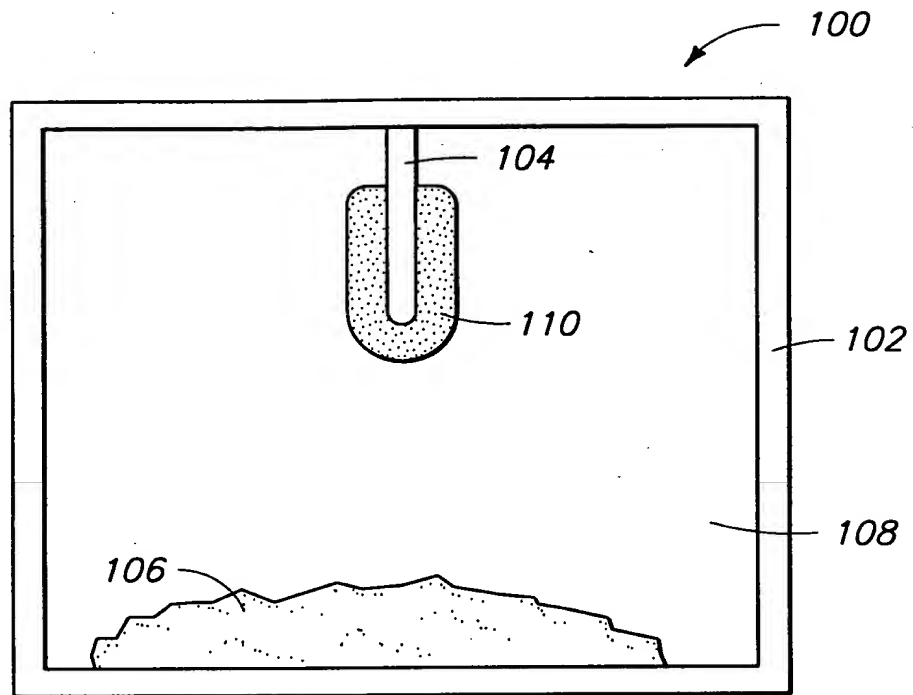
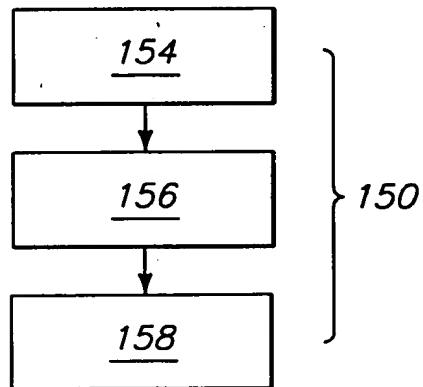
FIG. 2

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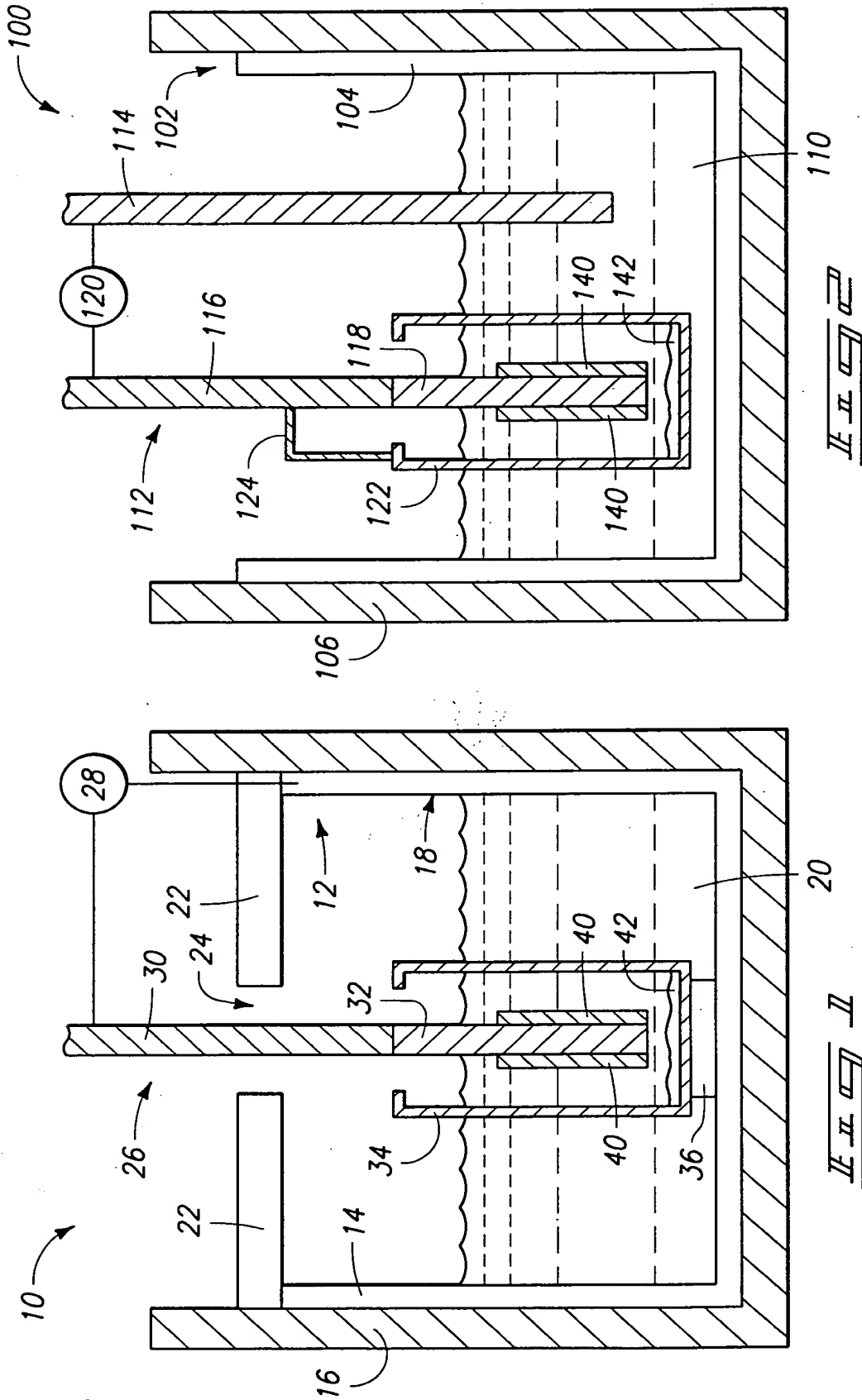


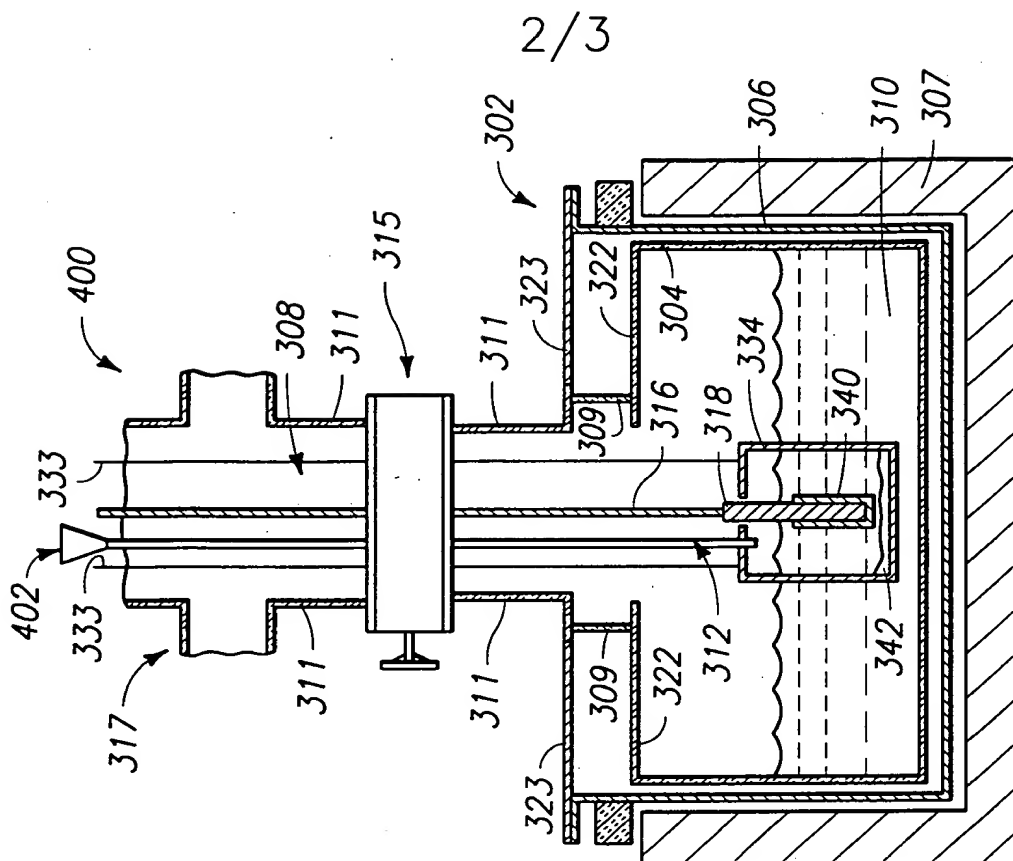
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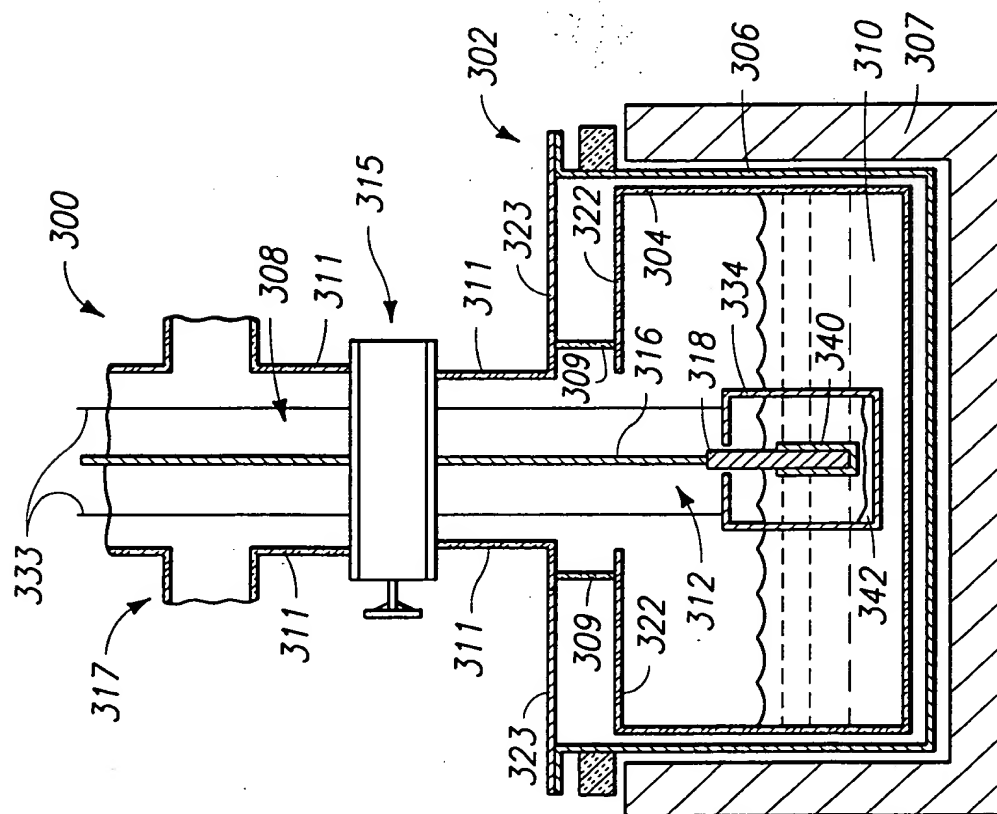
FIG. 5FIG. 6

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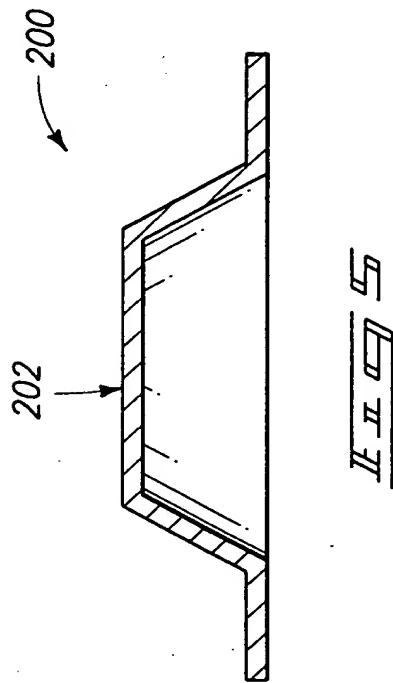
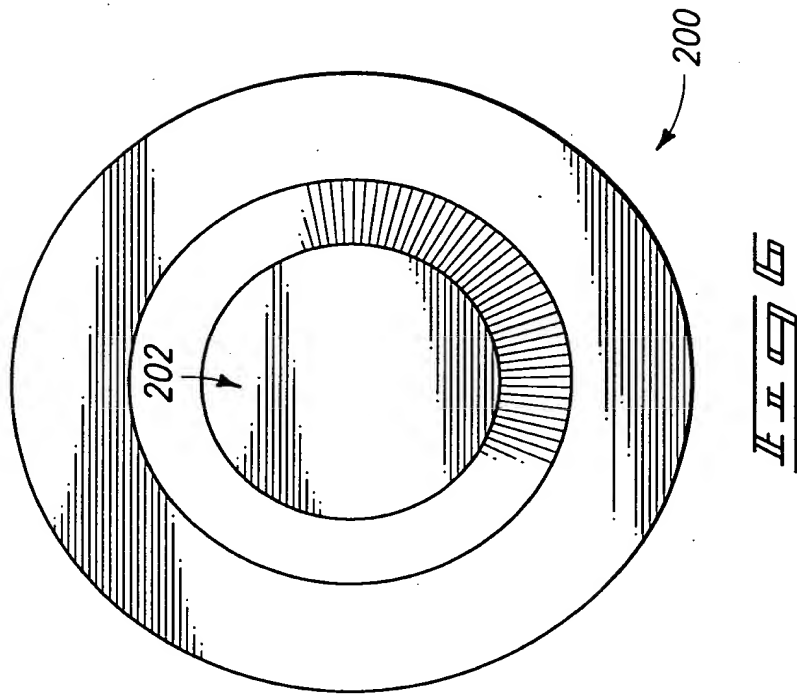


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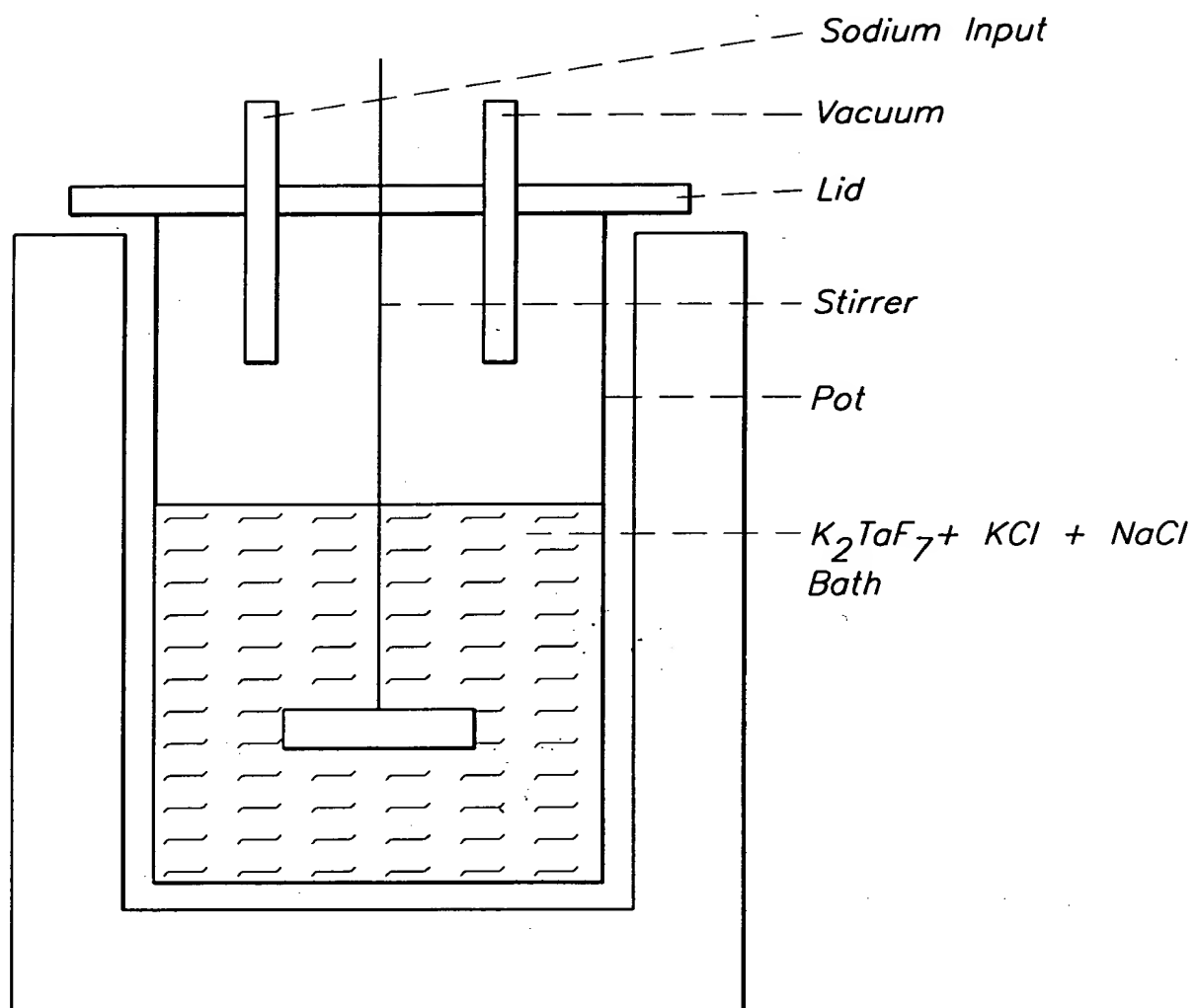


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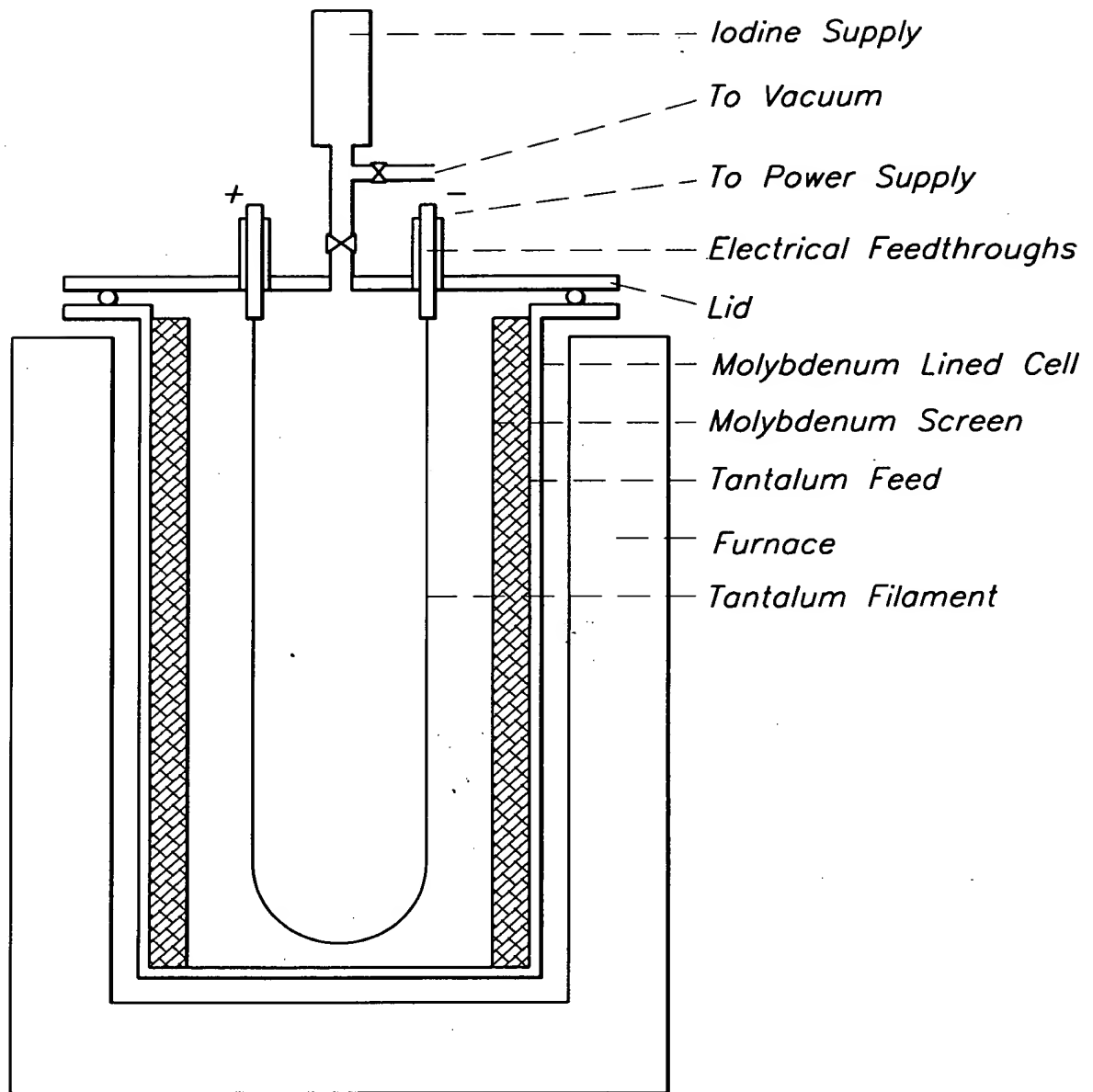
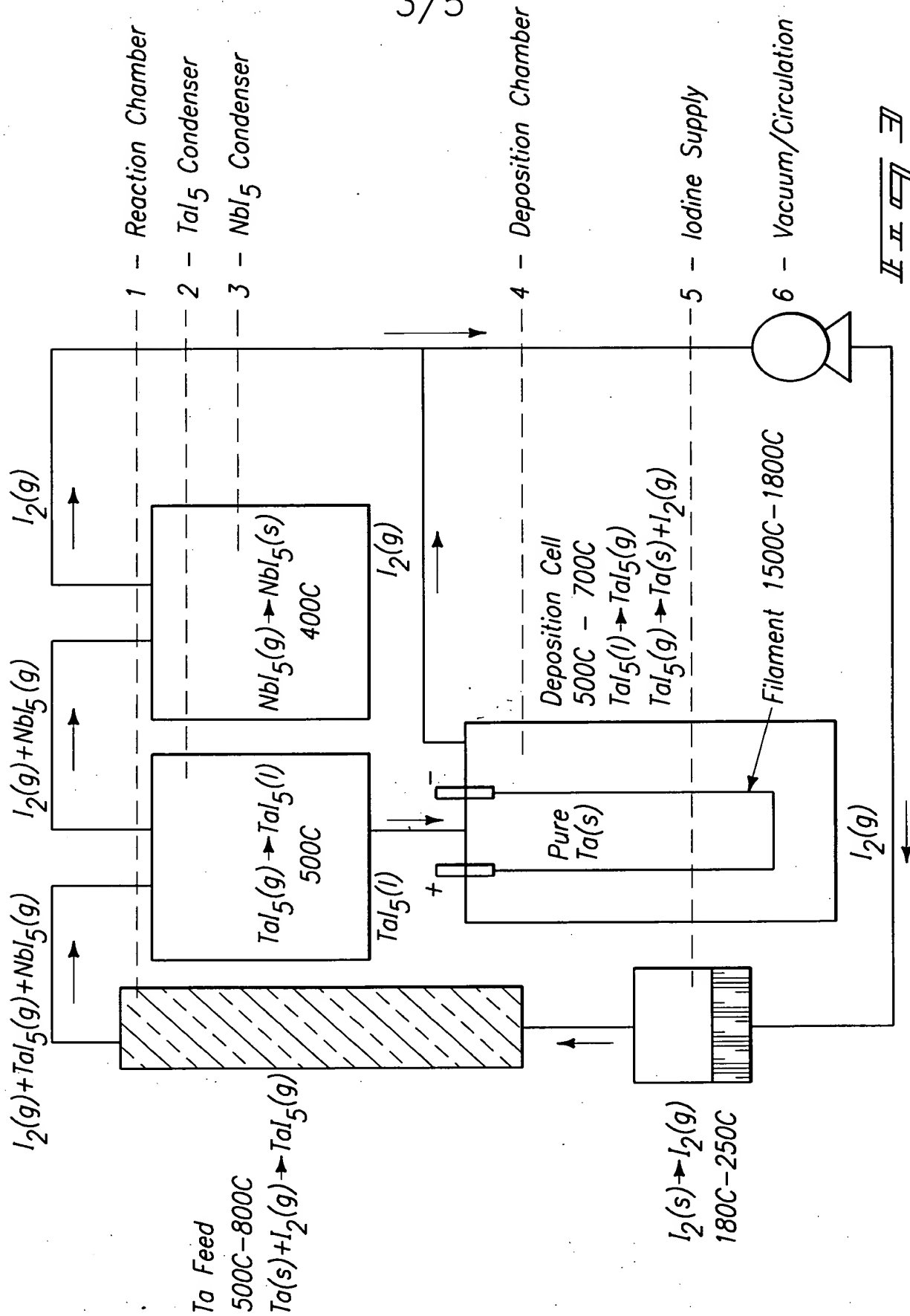
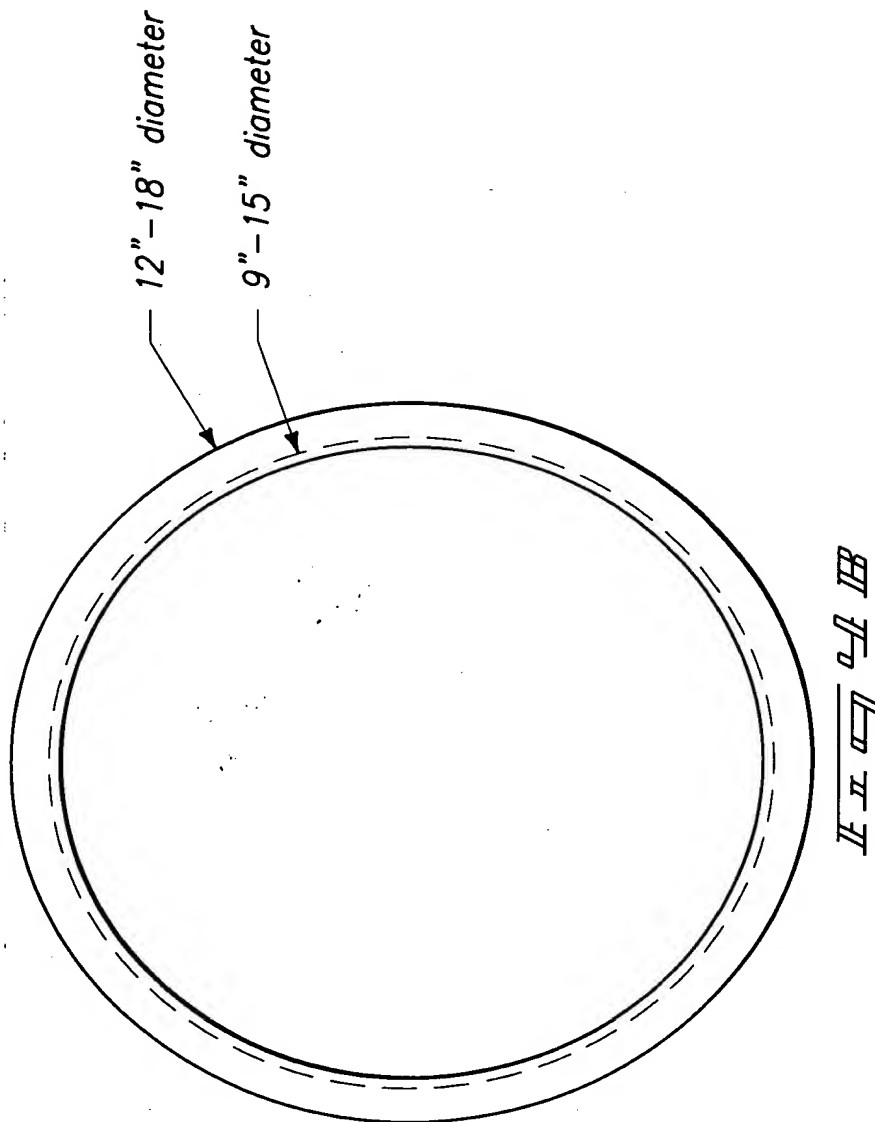
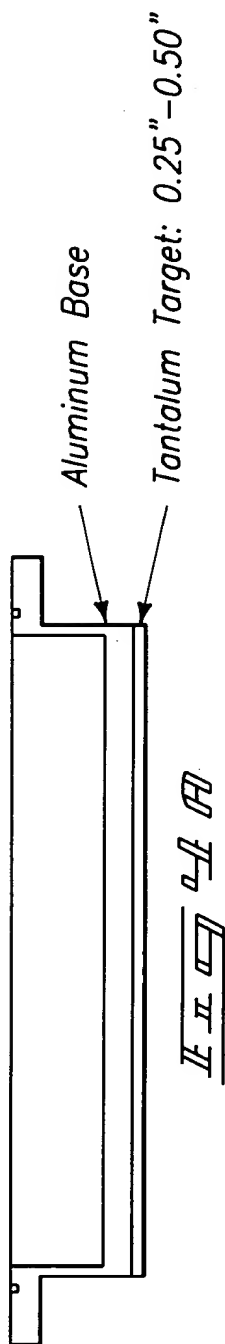


Fig 2

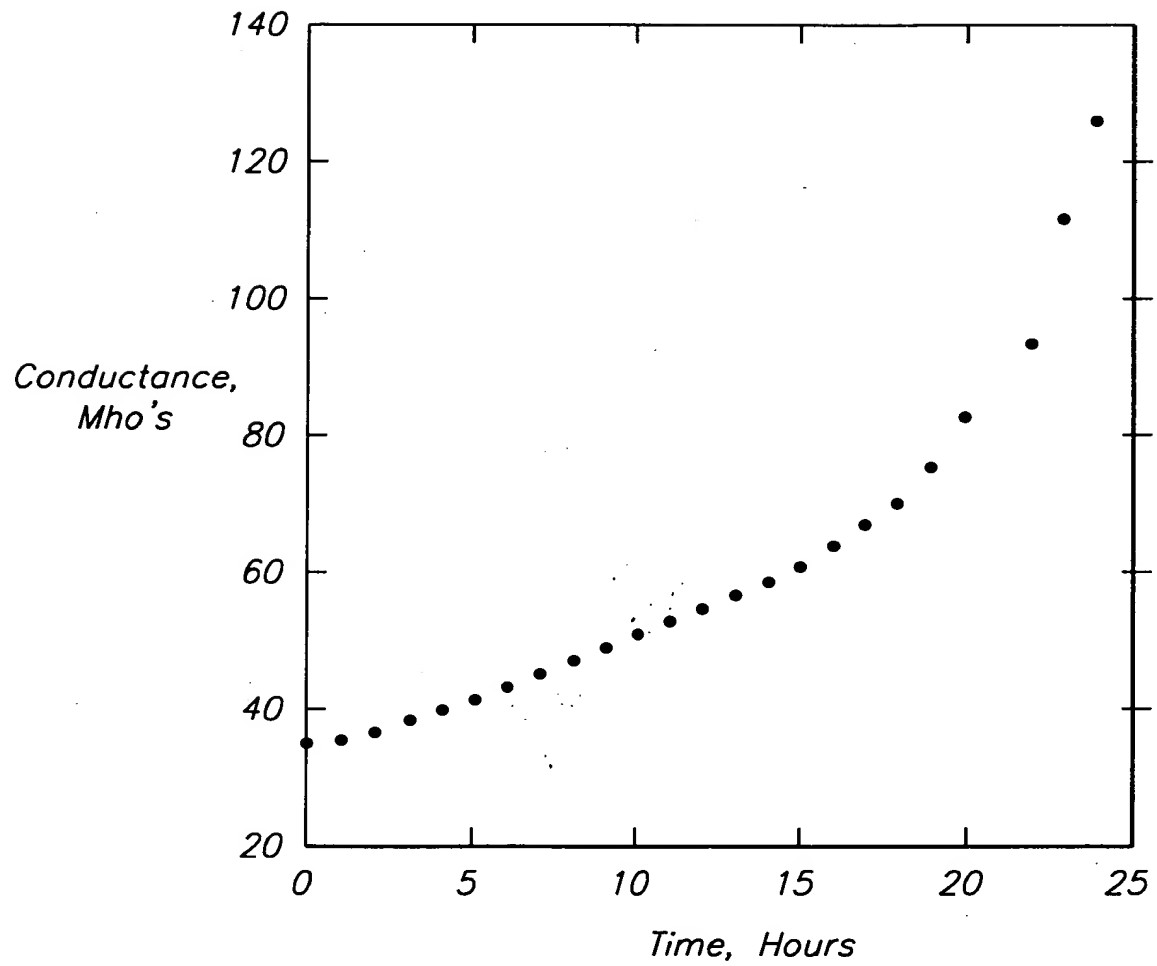
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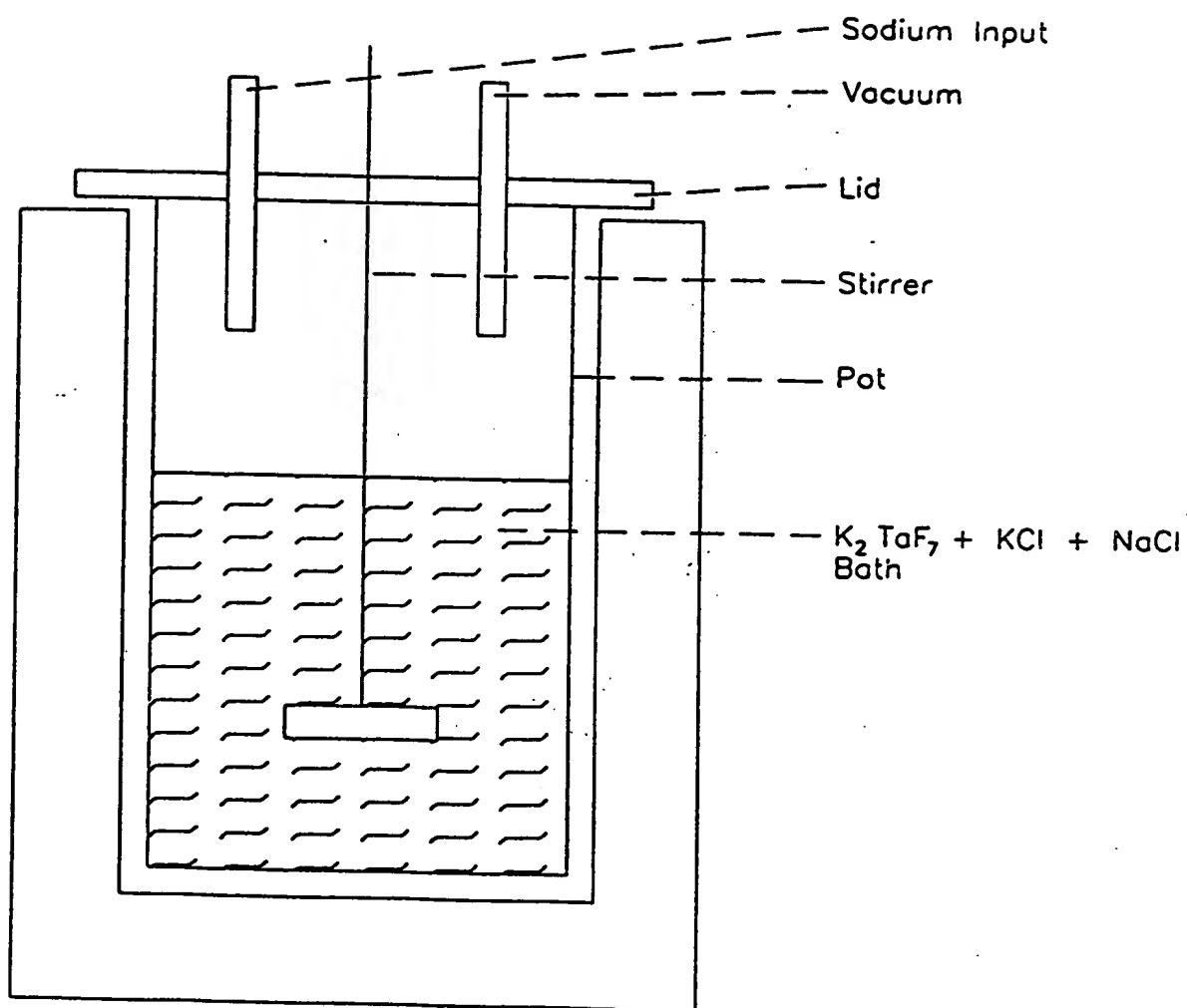


FIG. 1

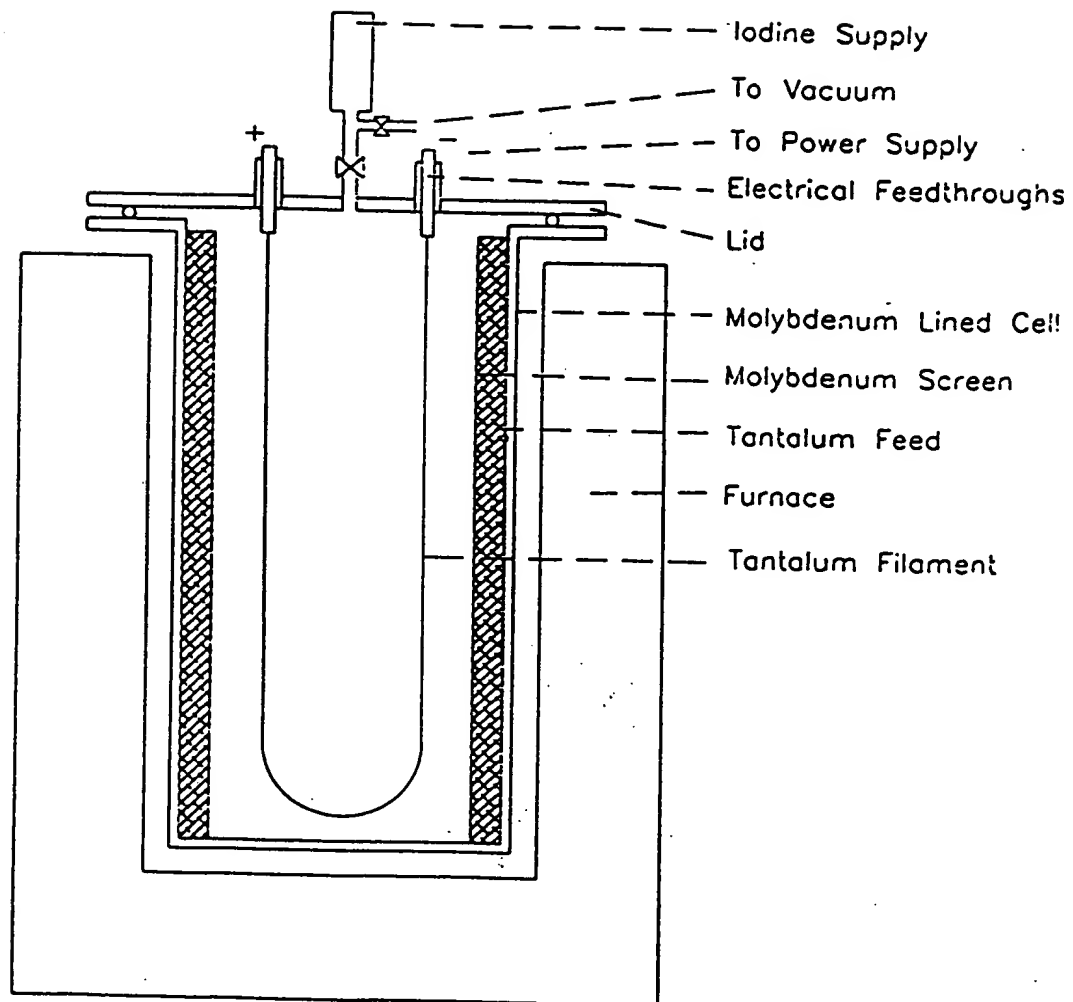


FIG. 2

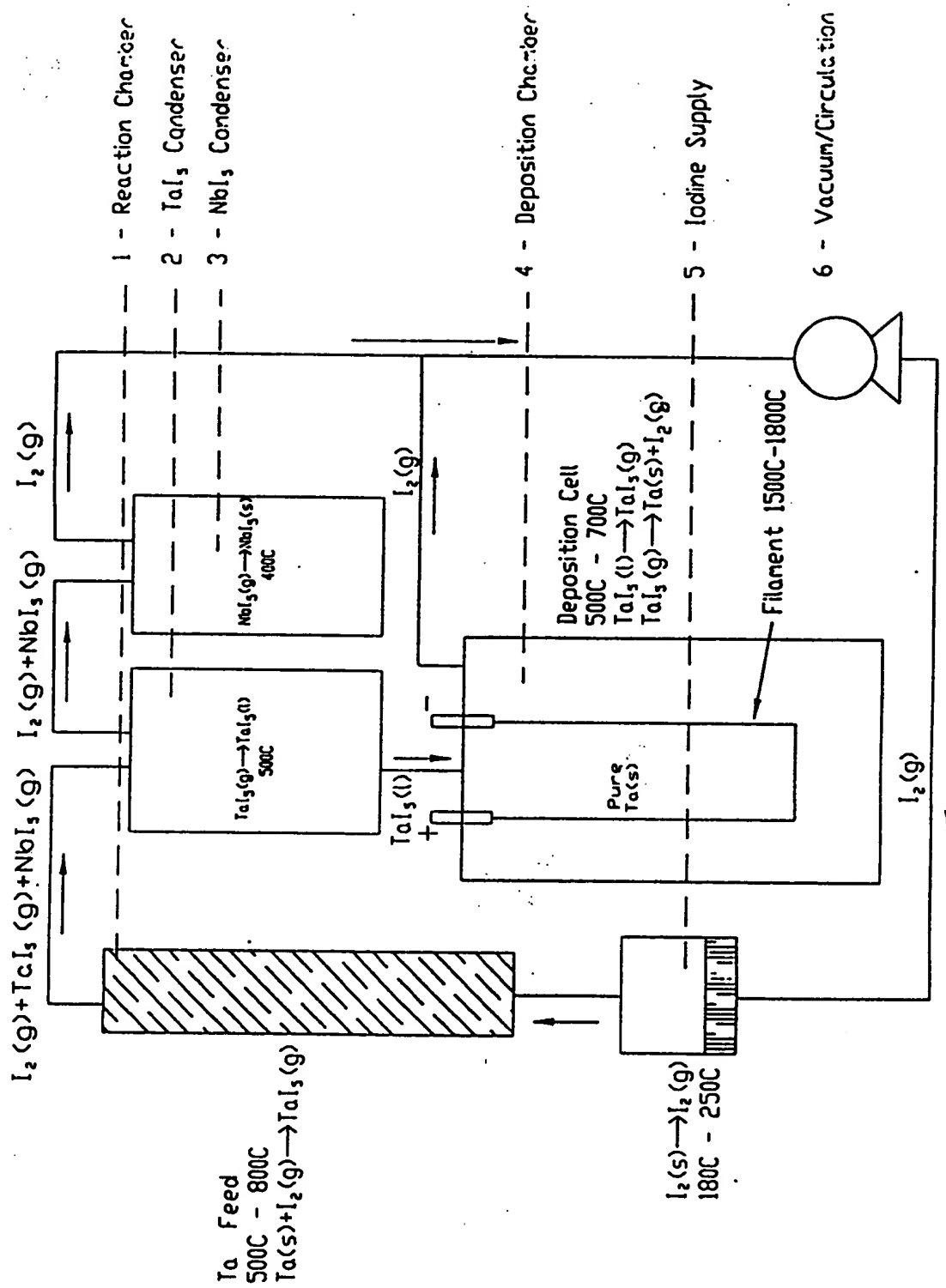


FIG. 3

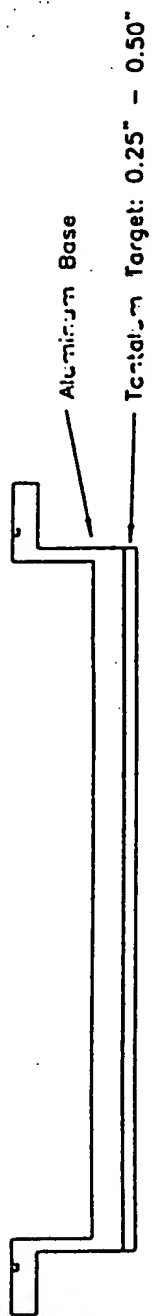


FIG. 4A

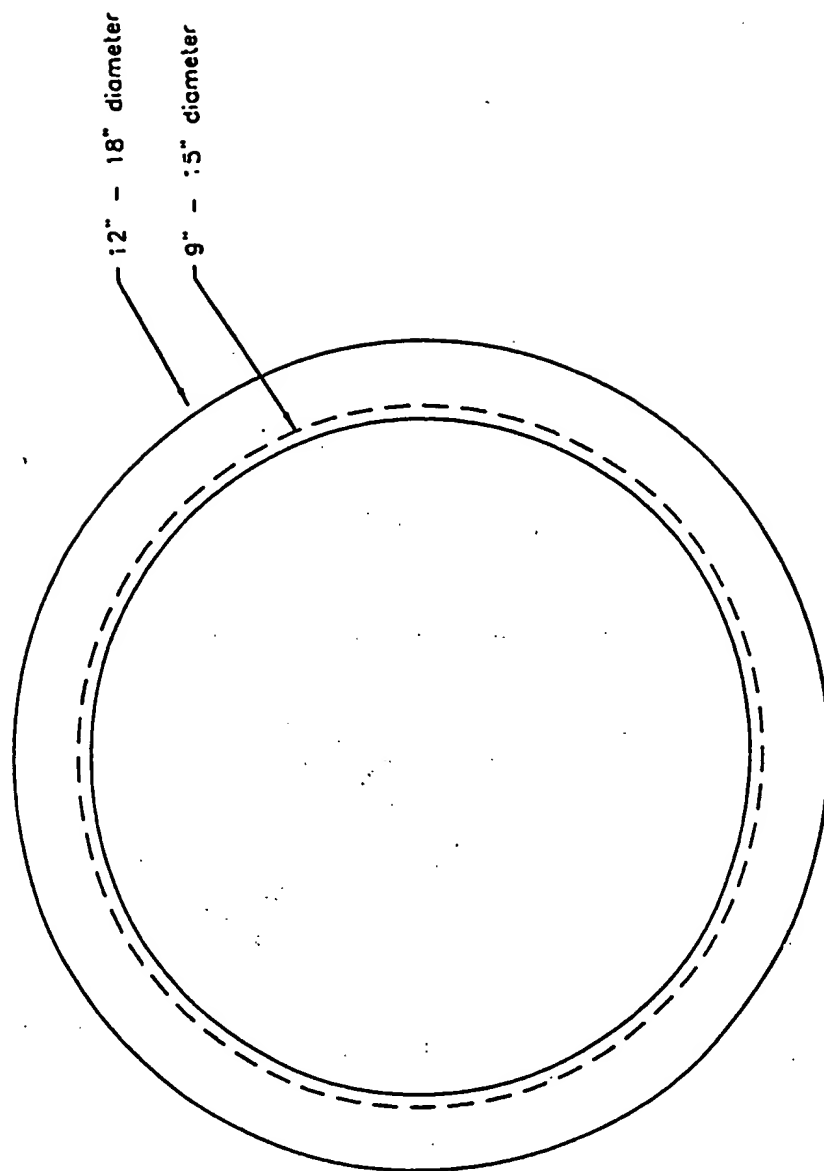


FIG. 4B

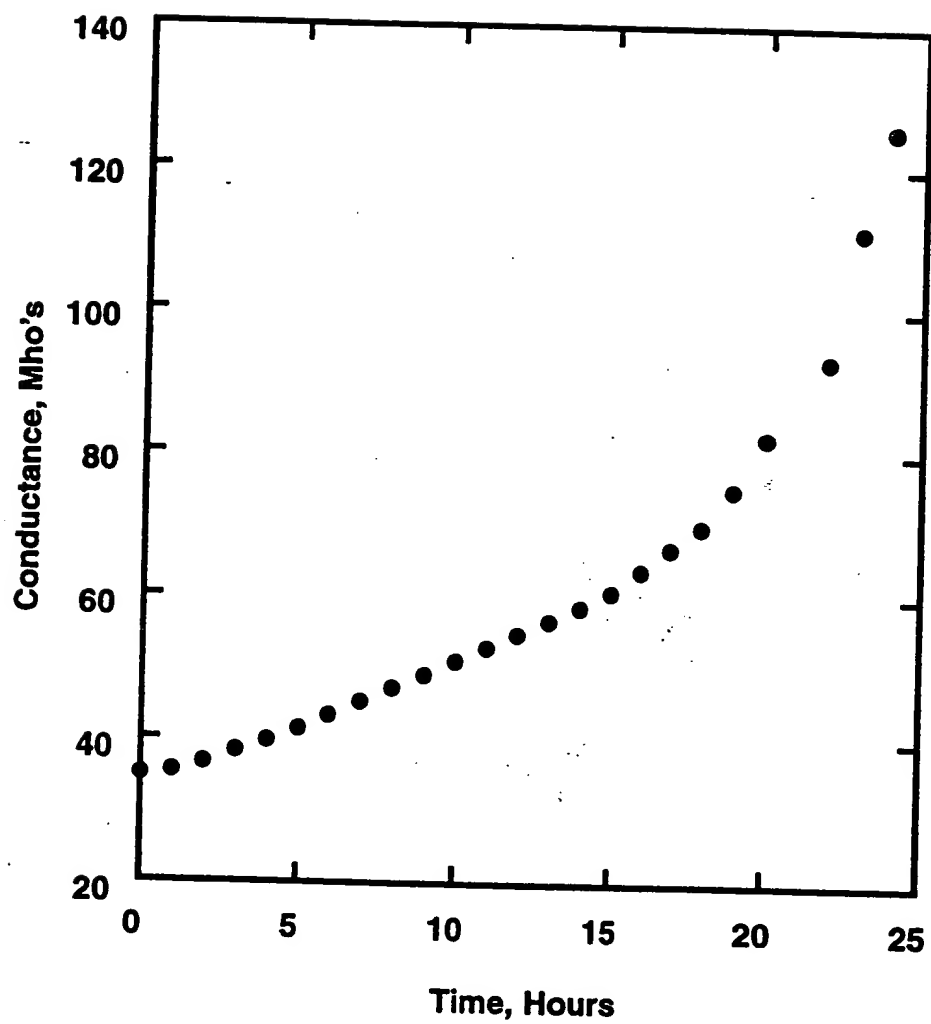


FIG. 5